

For Reference

NOT TO BE TAKEN FROM THIS ROOM

Ex libris
UNIVERSITATIS
ALBERTAENSIS



THE UNIVERSITY OF ALBERTA

RELEASE FORM

NAME OF AUTHOR ..Daniel Denis Poulin.....
TITLE OF THESIS ..Chemistry of Some Trifluoromethylphosphoranes
.....
.....
DEGREE FOR WHICH THESIS WAS PRESENTEDM.Sc.....
YEAR THIS DEGREE GRANTED1973.....

Permission is hereby granted to THE UNIVERSITY OF
ALBERTA LIBRARY to reproduce single copies of this
thesis and to lend or sell such copies for private,
scholarly or scientific research purposes only.

The author reserves other publication rights, and
neither the thesis nor extensive extracts from it may
be printed or otherwise reproduced without the author's
written permission.



Digitized by the Internet Archive
in 2019 with funding from
University of Alberta Libraries

<https://archive.org/details/Poulin1973>

THE UNIVERSITY OF ALBERTA

CHEMISTRY OF SOME TRIFLUOROMETHYLPHOSPHORANES

by



DANIEL DENIS POULIN

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILMENT OF THE REQUIREMENTS FOR THE DEGREE
of

MASTER OF SCIENCE

DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

Spring 1973

THE UNIVERSITY OF ALBERTA
FACULTY OF GRADUATE STUDIES AND RESEARCH

The undersigned certify that they have read, and
recommend to the Faculty of Graduate Studies and
Research for acceptance, a thesis entitled

"CHEMISTRY OF SOME TRIFLUOROMETHYLPHOSPHORANES"

submitted by DANIEL DENIS POULIN in partial ful-
filment of the requirements for the degree of
Master of Science.

A MES PARENTS

A B S T R A C T

Tris(trifluoromethyl)dichlorophosphorane reacts with dimethylamine to form tris(trifluoromethyl)bis(dimethylamino)phosphorane which is a relatively volatile white solid at room temperature. Reactions of the new phosphorane with HCl , $(\text{CH}_3)_2\text{NH}$, CCl_3H , CH_3OH , CH_3SH and H_2S were studied. The ^{19}F and ^1H nmr spectra indicated that the most probable structure for this phosphorane at low temperature is a trigonal bipyramidal structure in which the two dimethylamino groups occupy the equatorial positions. A process such as pseudorotation provides a means of averaging the CF_3 and $\text{N}(\text{CH}_3)_2$ environments within themselves at ordinary temperatures. Tris(trifluoromethyl)-chlorodimethylaminophosphorane was isolated from the reaction of tris(trifluoromethyl)dichlorophosphorane with lesser amounts of dimethylamine.

Pyrolysis of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ at 100°C gave bis(trifluoromethyl)bis(dimethylamino)fluorophosphorane whereas at 215°C trifluoromethyl bis(dimethylamino)difluorophosphorane was formed. The dimer $(\text{CF}_2)_2$ and the trimer $(\text{CF}_2)_3$ were also formed.

The reaction of $(\text{CF}_3)_2\text{PCl}_3$ with dimethylamine led to the isolation of bis(trifluoromethyl)dimethylaminodichlorophosphorane and trifluoromethyltris(dimethylamino)-phosphonium chloride. The latter compound was also

produced from the reaction of CF_3PCl_4 with excess dimethylamine.

Low temperature ^{19}F nmr studies of the reaction products of $(\text{CF}_3)_3\text{P}$ and Br_2 yielded nmr parameters for tris-(trifluoromethyl)dibromophosphorane. Attempts to resolve the different CF_3 environments in $(\text{CF}_3)_3\text{PCl}_2$, $(\text{CF}_3)_2\text{PCl}_3$ and $(\text{CF}_3)_3\text{PBr}_2$ using low temperature nmr were unsuccessful.

A C K N O W L E D G E M E N T S

The author wishes to express sincere thanks to his research supervisor, Dr. R. G. Cavell, for his assistance and direction, and to all the members of his research group for their helpful discussions.

Much gratitude is due to Mrs. M. Waters for preparation of this manuscript.

The author is grateful for the contribution of the technical staff of the Department of Chemistry and especially to Mr. T. Brisbane and Mrs. M. Tychkowsky for nmr spectra and to Mr. A. I. Budd for mass spectra.

Financial assistance from the University of Alberta and the National Research Council is gratefully acknowledged.

T A B L E O F C O N T E N T S

	<u>Page</u>
Abstract	v
Acknowledgements	vii
Table of Contents	viii
List of Tables	xi
List of Figures	xiii
 <u>CHAPTER I</u>	 1
Introduction	1
 <u>CHAPTER II</u>	 7
Materials, Apparatus and Techniques	7
1. High Vacuum Techniques	7
2. Reaction Conditions	7
3. Materials	9
4. Instrumental Techniques	9
 <u>CHAPTER III</u>	 11
Tris(trifluoromethyl)bis(dimethylamino)phos- phorane $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and tris(trifluoro- methyl)chlorodimethylaminophosphorane $(\text{CF}_3)_3\text{PClN}(\text{CH}_3)_2$	11
1. Preparation and Characterization of Tris- (trifluoromethyl)bis(dimethylamino)phos- phorane	11
2. Reactions of Tris(trifluoromethyl)bis- (dimethylamino)phosphorane	12

3. Preparation and Characterization of Tris-(trifluoromethyl)chlorodimethylamino-phosphorane	19
4. Reactions of Tris(trifluoromethyl)chloro-dimethylaminophosphorane.	23
5. Results and Discussion	24
<u>CHAPTER IV</u>	39
The Pyrolysis of Tris(trifluoromethyl)bis(di-methylamino)phosphorane $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$	39
1. Preparation and Characterization of bis-(trifluoromethyl)bis(dimethylamino) fluoro-phosphorane $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$	39
2. Preparation and Characterization of Tri-fluoromethylbis(dimethylamino)difluoro-phosphorane $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$	46
3. Results and Discussion.	48
<u>CHAPTER V.</u>	58
Reactions of Bis(trifluoromethyl)trichlorophos-phorane $(\text{CF}_3)_2\text{PCl}_3$ and Trifluoromethyltetra-chlorophosphorane CF_3PCl_4 with Dimethylamine	58
1. Preparation and Characterization of bis-(trifluoromethyl)dimethylaminodichloro-phosphorane $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$	58

	<u>Page</u>
2. Preparation and Characterization of Tri- fluoromethyltris(dimethylamino)phosphonium chloride $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$	63
3. Reactions of $(\text{CF}_3)_2\text{PCl}_3$ and $(\text{CH}_3)_2\text{NH}$	67
4. Reactions of CF_3PCl_4 and $(\text{CH}_3)_2\text{NH}$	68
5. Results and Discussion.	68
<u>CHAPTER VI</u>	80
Collected NMR Data and Structural Considerations	80
1. Preparation of $\text{CF}_3\text{P}(\text{S})\text{N}(\text{CH}_3)_2\text{Cl}$ and $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$	80
2. Preparation of $\text{CF}_3\text{P}(\text{O})\text{N}(\text{CH}_3)_2\text{Cl}$ and $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$	81
3. Preparation of $(\text{CF}_3)_3\text{PBr}_2$	81
4. Results and Discussion.	82
REFERENCES	90

L I S T O F T A B L E S

<u>Table</u>	<u>Page</u>
I Previously Prepared Trifluoromethylphosphor- anes	4
II Infrared Spectra of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$	13
III Mass Spectrum of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$	14
IV Mass Spectrum of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$	21
V Reaction Products of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and CH_3SH	35
VI Infrared Spectra of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ and $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$	41
VII Mass Spectra of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ and $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$	43
VIII The ir Spectrum of $(\text{CF}_3)_2\text{Cl}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$	60
IX The Mass Spectrum of $(\text{CF}_3)_2\text{Cl}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$	61
X The ir Spectra of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{PF}_6^-$ and $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-/\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$	65
XI Mass Spectrum of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{PF}_6^-$	66

<u>Table</u>	<u>Page</u>
XII Reaction Products of $(\text{CF}_3)_2\text{PCl}_3$ with $(\text{CH}_3)_2\text{NH}$	69
XIII Summary of the nmr Parameters of the Compounds Prepared in this Study	88

L I S T O F F I G U R E S

<u>Figure</u>		<u>Page</u>
1.	Gas Phase Reactor	8
2.	Fragmentation Pattern of the Unobserved Parent Phosphorane $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$	15
3.	The ^1H and ^{19}F nmr Spectra of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$	27
4.	Temperature Dependence of the ^{19}F nmr Spectra of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$	29
5.	The ^1H and ^{19}F nmr Spectra of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$	52
6.	Temperature Dependence of the ^{19}F nmr Spectra of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$	54
7.	Graphic Representation of the Reaction of $(\text{CF}_3)_2\text{PCl}_3$ with $(\text{CH}_3)_2\text{NH}$	70
8.	Possible Products from $(\text{CF}_3)_2\text{PCl}_3/(\text{CH}_3)_2\text{NH}$ Reactions	72
9.	The ^1H and ^{19}F nmr Spectra of $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$	77

CHAPTER II N T R O D U C T I O N

In recent years the chemistry of pentacoordinate compounds has attracted increasing attention, much of which has been directed toward an understanding of their bonding and stereochemistry.¹⁻⁶ Hybridization theory as well as electrostatic arguments suggest that two structures are energetically feasible for the pentacoordinate framework; the trigonal bipyramid and square pyramidal structures.⁷ Using the d_{z^2} as the d component orbital of a sp^3d hybrid results in the formation of the trigonal bipyramid structure whereas utilization of $d_{x^2-y^2}$ results in a square pyramidal structure.⁸ In each of these structures two different ligand environments exist; in the case of the trigonal bipyramid there is a set of two "axial" substituents and a set of three "equatorial" substituents whereas the square pyramidal structure offers a unique "axial" substituent and a set of four equivalent "pseudo-equatorial" or "basal" substituents. Bond lengths are not necessarily equal in the two sets of substituents, and the trigonal bipyramidal arrangement provides longer bonds in the "axial" directions, an observation which can be rationalized by considering the interactions of bond pairs with neighboring ligands following the rules of Gillespie.⁹ The axial bond pair has three nearest neighbors at 90° whereas the equatorial

bond pairs have only two such neighboring pairs, thus ⁹ equilibrium can only be attained if the axial pairs are at a greater distance from the nucleus than the equatorial pairs. Theoretical calculations show ¹⁰ that maximum overlap of an orbital of the ligand atom with an equatorial orbital of the central atom occurs at a slightly smaller internuclear distance than for axially substituted atoms. Thus both approaches suggest that axial bonds in a trigonal bipyramid are expected to be longer than equatorial bonds.

Muetterties et al ¹¹, in their study of pentacoordinate phosphoranes, found that the most electronegative substituents tended to occupy the axial positions with only a few exceptions ^{12,13} which were attributed to extreme steric interactions. Recent calculations have suggested that ¹⁴ the back-bonding into the d-orbitals of the central atom is more effective from the equatorial than from the apical position. Thus the apicophilicity ¹⁴ of a given group becomes a balance between electronegativity, increase in which favors occupation of the apical position, and the ability to back-bond into the d-orbitals of the central atom, increase in which favors occupation of the equatorial positions, with steric factors playing an unknown role. ¹⁵

The wide range of known phosphoranes, their relative stability and their ease of preparation make the

pentacoordinated phosphorus system an ideal one for a study of the relative importance of the above effects. Fluoro- and trifluoromethylphosphoranes are conveniently studied by means of the built-in molecular probes provided by the 100% abundance of the ^{19}F and ^{31}P nuclei of spin 1/2 and good nmr sensitivity. Many fluorophosphoranes have been characterized, while the trifluoromethylphosphoranes previously known (Table I) are relatively few in number. The electronegativity^{16,17} of the F and CF_3 groups implies a strong inductive withdrawal of electrons and an apicophilic behavior. Whereas this tendency is reinforced by the lack of back-bonding capabilities for CF_3 ¹⁸, the considerable back-bonding ability of fluorine¹⁸ tends to reduce its apicophilic character.

Most of the compounds in Table I follow the stereochemistry predicted from the relative electronegativity¹¹ of the substituents except for that of $(\text{CF}_3)_2\text{PF}_3$ and CF_3PF_4 where some conflict in ir and microwave results exists and the structures suggested differ from those predicted. These results present however an unsolved problem.

The stereochemical conclusions based on nmr measurements at temperatures where intramolecular motion can cause chemical equivalence may be somewhat equivocal since, as outlined by Ugi and Ramirez¹⁹, equivalence of substituent groups can be effected quite simply by means of

TABLE I

Previously Prepared Trifluoromethylphosphoranes

<u>Compound</u>	<u>Synthesis</u>	<u>Structure</u>	<u>Method</u>
$(\text{CF}_3)_3\text{PCl}_2$	$(\text{CF}_3)_3\text{P} + \text{Cl}_2$ ²⁰		
$(\text{CF}_3)_2\text{PCl}_3$	$(\text{CF}_3)_2\text{PCl} + \text{Cl}_2$ ²¹	ax-2CF ₃	ir, Raman ²²
CF_3PCl_4	$(\text{CF}_3)\text{PCl}_2 + \text{Cl}_2$ ²³	ax-1CF ₃	ir, Raman ²⁴
$(\text{CF}_3)_2\text{PBr}_3$	$(\text{CF}_3)_2\text{PBr} + \text{Br}_2$ ²⁵		
$(\text{CF}_3)_3\text{PBr}_2$	$(\text{CF}_3)_3\text{P} + \text{Br}_2$ ²⁵		
$(\text{CF}_3)_3\text{PF}_2$	$(\text{CF}_3)_3\text{P} + \text{SF}_4$ ²⁶	eq-3CF ₃	nmr ¹¹ (a)
$(\text{CF}_3)_2\text{PF}_3$	$(\text{CF}_3)_2\text{PCl}_3 + \text{SbF}_3$ ²⁶	ax-2CF ₃	nmr ¹¹ (a)
CF_3PF_4	$\text{CF}_3\text{PCl}_4 + \text{SbF}_3$ ²⁶	eq-CF ₃	ir ²⁷
		ax-CF ₃	microwave ²⁸
$\text{CF}_3\text{PCl}_3\text{F}$	$\text{CF}_3\text{PCl}_2 + \text{ClF}$ ²⁹	ax-CF ₃	nmr ²⁹ (a)
$(\text{CF}_3)_2\text{P}[\text{ON}(\text{CF}_3)_2]_3$	$(\text{CF}_3)_2\text{PH} + (\text{CF}_3)_2\text{NO}$ ³⁰		
$(\text{CF}_3)_2\text{PCl}_2\text{N}(\text{CF}_3)_2$	$(\text{CF}_3)_2\text{PN}(\text{CF}_3)_2 + \text{Cl}_2$ ³¹		
$\text{CF}_3\text{PF}_2\text{Cl}_2$	$\text{CF}_3\text{PF}_2 + \text{Cl}_2$ ³²	eq-CF ₃	nmr ³² (a)
$(\text{CF}_3)_2\text{PFCl}_2$	$(\text{CF}_3)_2\text{PF} + \text{Cl}_2$ ³²		
$(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$	$(\text{CF}_3)_3\text{PO} + [\text{CH}_3)_3\text{Si}]_2\text{O}$ ³³	ax-2CF ₃ eq-1CF ₃	nmr ³³ (continued...)

TABLE I (continued)

$\text{CF}_3\text{PF}_3\text{CH}_3$	$\text{CF}_3\text{PF}_4 + (\text{CH}_3)_4\text{Sn}$ ³⁴	eq-CF ₃	nmr	34
$(\text{CF}_3)_2\text{PF}_2\text{CH}_3$	$(\text{CF}_3)_2\text{PF}_3 + (\text{CH}_3)_4\text{Sn}$ ³⁴	eq-2CF ₃	nmr	34
$\text{CF}_3\text{PF}_3\text{N}(\text{CH}_3)_2$	$\text{CF}_3\text{PF}_4 + (\text{CH}_3)_2\text{NSi}(\text{CH}_3)_3$ ³⁴	eq-CF ₃	nmr	34
$(\text{CF}_3)_2\text{PF}_2\text{N}(\text{CH}_3)_2$	$(\text{CF}_3)_2\text{PF}_3 + (\text{CH}_3)_2\text{NSi}(\text{CH}_3)_3$ ³⁴	eq-2CF ₃	nmr	34

(a) Conclusion equivocal - see text

ax = axial

eq = equatorial

either turnstile rotation or Berry pseudorotation. These processes can be quenched upon cooling and it is necessary to carry out these measurements below the quenching temperature if reliable stereochemical conclusions are to be obtained.

It can be seen from Table I that the stereochemistry of trifluoromethylphosphoranes is still in a state of some uncertainty. Our work, which deals primarily with the preparation and characterization of phosphoranes containing various substituents of substantially different electronegativities and back-bonding capabilities was undertaken in an attempt to provide avenues of possible further insight into the factors discussed above.

CHAPTER II

MATERIALS, APPARATUS AND TECHNIQUES

1. High Vacuum Techniques

Due to the air and moisture sensitivity of many of the reactants and reaction products all manipulations were carried out using standard high vacuum techniques. Separation of volatile compounds was usually achieved by passing them through a series of traps cooled with slush baths to various temperatures. This procedure is referred to in the text as vacuum fractionation. The vacuum system was constructed with Pyrex glass and the stopcocks lubricated with Apiezon N grease. Involatile materials which remained in the reaction vessel following vacuum fractionation were handled in a nitrogen atmosphere while aqueous solutions were handled in the air since it had been found by experience that such products were invariably air stable.

2. Reaction Conditions

Reactions were generally carried out in sealed Pyrex glass tubes of approximate volumes 10, 25 or 75cc depending on the scale of the reaction and the maximum calculated pressure expected. Reaction temperatures are quoted in the appropriate sections. A special gas phase reactor (Figure I) was constructed for a series of reactions described in Chapters III and V.

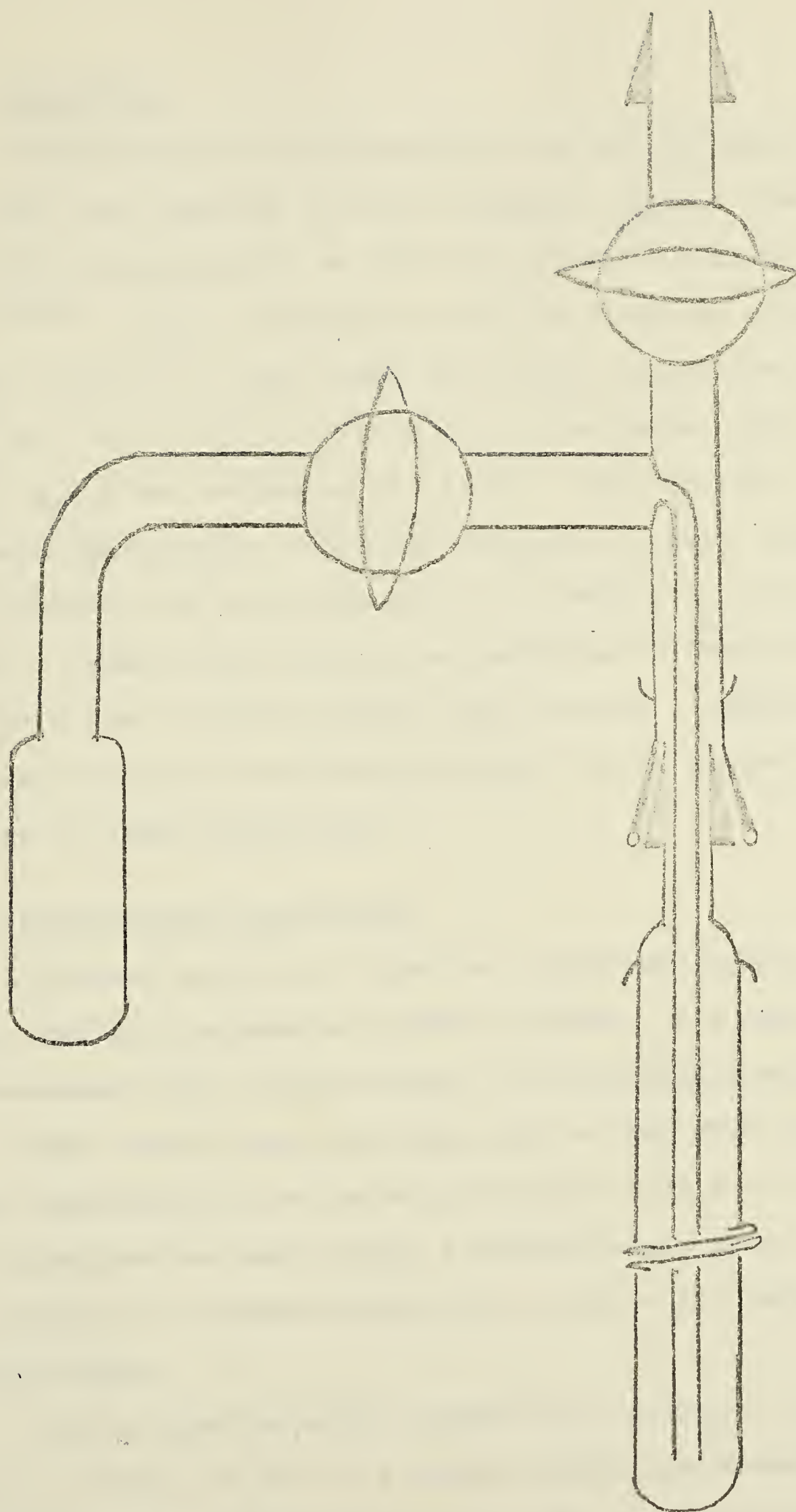


FIGURE 1 Gas Phase Reactor

3. Materials

Trifluoromethyliodophosphines and $(\text{CF}_3)_3\text{P}$ were prepared from the reaction of CF_3I (Columbia Organic Chemical Co.) with red phosphorus at 220°C for 48 hrs in glass Carius tubes.^{20,35} Vacuum fractionation of the volatile products through a series of cold traps gave CF_3PI_2 which was collected at -45°C , $(\text{CF}_3)_2\text{PI}$ which was collected at -84°C and $(\text{CF}_3)_3\text{P}$ which was collected at -116°C . The remaining trifluoromethylphosphorus compounds required in this study were prepared from these phosphines according to literature methods. Commercially available chemicals of "Reagent" grade were used without further purification. Reagent gases were usually fractionated before use to remove any moisture or gross impurities.

4. Instrumental Techniques

Infrared spectra of gases were obtained using a 9 cm gas cell with potassium bromide windows. All spectra were recorded with a Perkin-Elmer 457 spectrophotometer.

Mass spectra were recorded with an AEI MS-9 spectrometer operating at an ionizing voltage of 70 e.v. Samples were introduced as gases using a heated inlet, as low volatile liquids in a heated capillary, or as solids using a direct probe.

All nmr spectra were recorded with either a Varian A56/60, a Varian HA 100 or a Bruker HFX-90 spectrometer. Proton spectra were recorded at 60.0 MHz and fluorine

spectra at 56.4 MHz using the A56/60 instrument. In the case of the HA 100 instrument, proton spectra were recorded at 100 MHz, fluorine spectra at 94.1 MHz while for the Bruker the proton spectra were recorded at 90 MHz and the fluorine spectra at 84.67 MHz. Samples for nmr measurements of volatile products were prepared under vacuum by distilling an appropriate quantity of the compound and sufficient solvent into 5 mm o.d. medium wall sample tube. Proton and fluorine spectra were routinely recorded on samples containing an approximate 10% solution of the compound in CFCl_3 or CF_2Cl_2 . Nmr measurements for involatile products were obtained in solutions of CH_2Cl_2 , CHCl_3 , CD_3CN or H_2O . Samples which were volatile and air sensitive were made up in sealed tubes as dilute solutions in CFCl_3 and the fluorine chemical shifts were measured relative to the internal CFCl_3 with the proton chemical shift measured relative to external tetramethylsilane (TMS). Compounds which were either involatile or air stable or both were dissolved in a suitable solvent and the chemical shifts of fluorine and hydrogen were measured relative to CFCl_3 and TMS provided in a single capillary containing a 5% solution of TMS in CFCl_3 . Each instrument was equipped with a variable temperature controller which appeared to be accurate to within $\pm 5^\circ\text{C}$ of the temperature indicated on the controller.

CHAPTER IIITRIS (TRIFLUOROMETHYL) BIS (DIMETHYLAMINO) PHOSPHORANE $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ AND TRIS (TRIFLUOROMETHYL) CHLORO-DIMETHYLAMINOPHOSPHORANE $(\text{CF}_3)_3\text{PClN}(\text{CH}_3)_2$

Pentacoordinate phosphorus compounds with at least one trifluoromethyl group have been known for a number of years (Table I). Only one trifluoromethyl phosphorus compound with five non-halogen substituents has been reported.³³ In this chapter the synthesis and characterization of two dimethylamino substituted pentacoordinate CF_3 phosphorus compounds are described.

1. Preparation and Characterization of Tris(trifluoromethyl)bis(dimethylamino)phosphorane.

(a) From $(\text{CF}_3)_3\text{PCl}_2$ and $(\text{CH}_3)_2\text{NH}$

Tris(trifluoromethyl)dichlorophosphorane, $(\text{CF}_3)_3\text{PCl}_2$ ²⁰ (1.390 g, 4.50 mmoles) and dimethylamine $(\text{CH}_3)_2\text{NH}$ (0.825 g, 18.30 mmoles) were allowed to react at room temperature for 72 hours. Vacuum fractionation gave $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (1.312 g, 4.02 mmoles) in 89.3% yield collected at -45°C . The phosphorane was obtained in 99% purity (by nmr).

$(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ ³⁶ (0.017 g, 0.08 mmoles) was found in the -84°C and -116°C traps. Dimethylamine (0.045 g, 1.00 mmoles) and CF_3H (0.027 g, 0.39 mmoles) were found in the -116°C and -196°C traps. The salt $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$ remained

as an involatile white solid in the reaction tube. In another reaction, when this salt was dissolved in a solution of 25% AgNO_3 , 96% of the chlorine in the original $(\text{CF}_3)_3\text{PCl}_2$ was recovered as AgCl .

(b) Characterization of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$

The compound is a white solid at room temperature which decomposes upon melting at 94°C . Decomposition also occurs over long periods of time at room temperature and will be discussed in more detail in Chapter 4.

The compound was characterized by its spectroscopic properties (ir Table II and nmr Table XIII) by mass spectroscopy (Table III) and by chemical reactions described below. The mass spectrum of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ showed no parent ion, a result which is typical of pentacoordinate phosphorus compounds.³⁷ The strong ions at 257 and 282 were identified by mass measurements (calcd for $(\text{CF}_3)_2\text{P}[\text{N}(\text{CH}_3)_2]_2^+$ m/e 257.0644; found m/e 257.0640; calcd for $(\text{CF}_3)_3\text{PN}(\text{CH}_3)_2^+$ m/e 282.0095; found m/e 282.0090:) and have a composition which strongly suggests that they arise from the fragmentation of the unobserved parent phosphorane $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ by loss of CF_3 and $\text{N}(\text{CH}_3)_2$ in the two pathways shown in Figure 2.

2. Reactions of Tris(trifluoromethyl)bis(dimethylamino) - phosphorane.

TABLE II

Infrared Spectra of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$

$(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ ^{a,b,c}	$(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ ^{a,b}	Assignment
3021 (vw)	3028 (vw)	} $\nu(\text{C-H})$
2943 (m)	2945 (w)	
2922 (w, sh)	2877 (w)	
2878 (w)	2828 (w)	
2824 (w)		
1463 (m)	1464 (w)	} $\delta(\text{CH}_3) \text{ \& } \nu_s(\text{C}_2\text{N})$
1375 (w)	1283	
1290 (m)		
1200 (s)	1205 (s)	} $\nu(\text{C-F})$
1150 (vs)	1182 (s)	
1129 (m, sh)	1152 (ms, sh)	
1092 (s)	1131 (s)	
987 (m)	988 (m)	$\nu_{as}(\text{C}_2\text{N})$
741 (w)	709 (m)	$\delta_s(\text{CF}_3)$
660 (m)	593 (m)	$\nu_{as}(\text{N}_2\text{P})$
562 (m)	578 (m)	} $\delta_{as}(\text{CF}_3)$
541 (w, sh)		
499 (w)	508 (m)	} $\nu(\text{P-CF}_3)$
	483 (m)	

(a) All values in cm^{-1}

(b) Abbreviations: ν = stretching, δ = deformation, s = strong, m = medium, w = weak, v = very, sh = shoulder, as = antisymmetric, s = symmetric.

(c) To increase the intensity of the peaks the ir cell was heated to 60°C .

TABLE III

Mass Spectrum of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ ^a

<u>m/e</u>	<u>rel. int.^b</u>	<u>assignment</u>	<u>m/e</u>	<u>rel. int.^b</u>	<u>assignment</u>
282 ^c	0.2	$\text{C}_5\text{F}_9\text{H}_6\text{NP}$	70	0.6	CF_3H , HF_2P
257 ^c	0.05	$\text{C}_6\text{F}_6\text{H}_{12}\text{N}_2\text{P}$	69	29.7	CF_3 , F_2P
229	0.7	$\text{C}_4\text{F}_7\text{H}_3\text{NP}$	64	0.9	$\text{C}_2\text{F}_2\text{H}_2$
213	1.8	$\text{C}_4\text{F}_6\text{H}_6\text{NP}$	60	0.7	CH_3NP
182	0.9	$\text{C}_4\text{F}_6\text{H}_6\text{N}$	57	3.0	CNP , F_3 , $\text{C}_3\text{H}_7\text{N}$
160	0.9	$\text{C}_3\text{F}_4\text{H}_3\text{NP}$	56	2.8	$\text{C}_3\text{H}_6\text{N}$
144	3.9	$\text{C}_3\text{F}_3\text{H}_6\text{NP}$	51	17.5	FHP
132	0.8	$\text{C}_3\text{F}_4\text{H}_6\text{N}$	50	4.9	CF_2 , FP
119	1.9	CF_4P	44	0.6	$\text{C}_2\text{H}_6\text{N}$
113	1.3	$\text{C}_3\text{F}_3\text{H}_6\text{N}$	43	2.3	$\text{C}_2\text{H}_5\text{N}$
112	1.7	$\text{C}_4\text{F}_2\text{H}_{12}\text{N}$	42	3.3	$\text{C}_2\text{H}_4\text{N}$
110	1.0	$\text{C}_2\text{F}_2\text{H}_3\text{NP}$	41	1.9	$\text{C}_2\text{H}_3\text{N}$
94	7.1	$\text{C}_2\text{FH}_6\text{NP}$	31	9.0	CF

(a) The parent ion $\text{C}_7\text{F}_9\text{H}_{12}\text{N}_2\text{P}^+$, m/e 326 was not observed.

(b) Intensities are expressed relative to the total ionization defined as $\sum(\text{intensity})$ for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak.

(c) The identity of these peaks was established by mass measurement under high resolution.

FIGURE 2

Fragmentation Pattern of the Unobserved Parent Phosphorane $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$

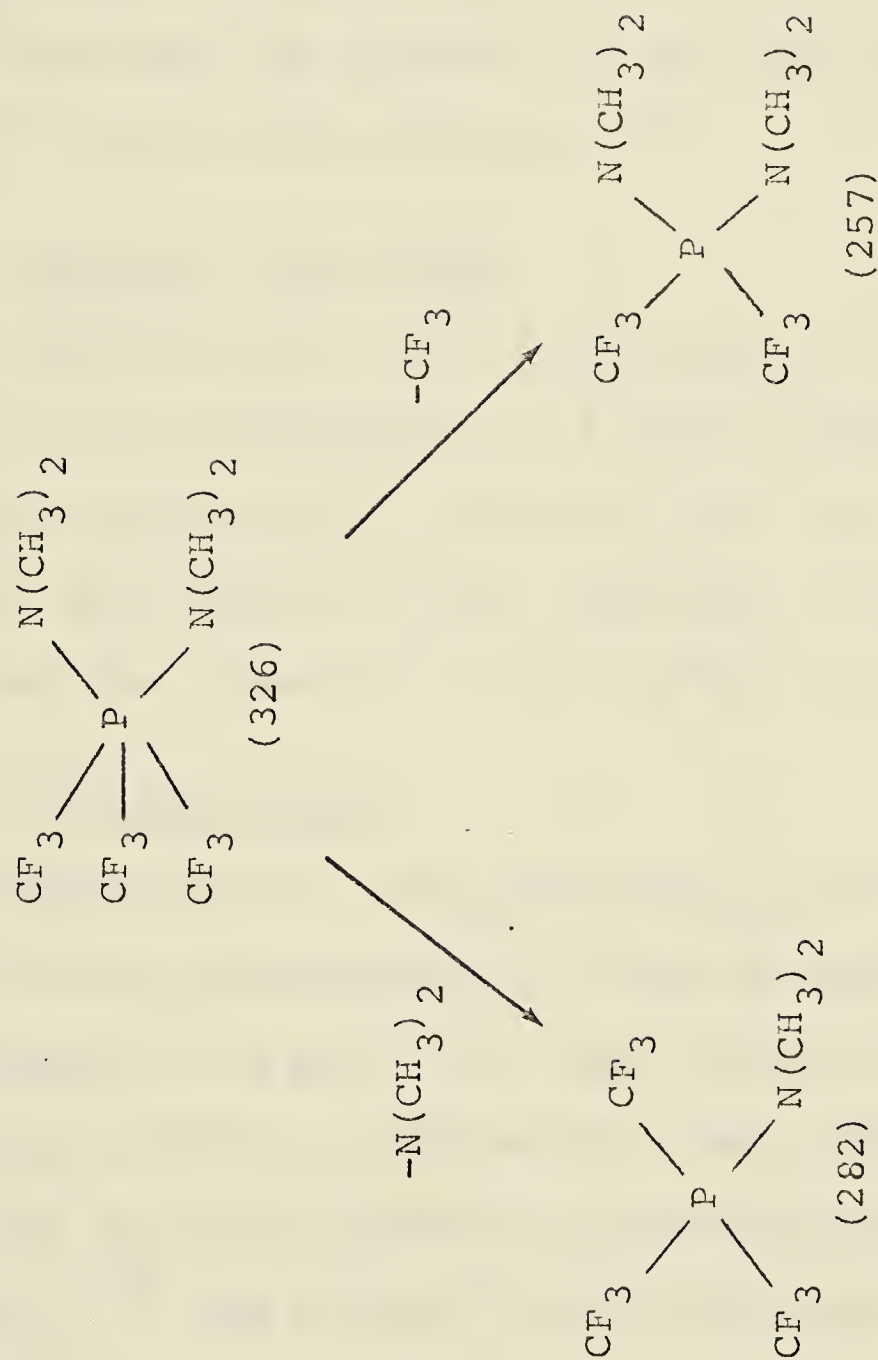


FIGURE 2 A possible mass spectral fragmentation pattern of the unobserved parent phosphorane $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$. Formulae of products have been established by accurate mass measurements however structures are only proposals.

(a) Neutral Hydrolysis

Hydrolysis of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.095 g, 0.29 mmoles) with approximately 0.8 mls of degassed distilled H_2O at room temperature for 24 hours gave CF_3H (0.029 g, 0.41 mmoles). Nmr spectra of the remaining aqueous solution indicated the presence of the $(\text{CF}_3)_2\text{PO}_2^-$ and $\text{CF}_3\text{PO}_3^{2-}$ ions in the ratio 2:1.³⁸

(b) Alkaline Hydrolysis

Hydrolysis of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.118 g, 0.36 mmoles) with approximately 0.8 mls of degassed 10% NaOH at room temperature for 24 hours gave CF_3H (0.052 g, 0.74 mmoles). Nmr spectra of the remaining aqueous solution indicated the presence of the $\text{CF}_3\text{PO}_3^{2-}$ ion.³⁸

(c) Acid Hydrolysis

Hydrolysis of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.126 g, 0.39 mmoles) with approximately 0.8 mls of degassed distilled H_2O adjusted to a pH $\approx$ 1 at room temperature for 24 hours gave CF_3H (0.029 g, 0.41 mmoles). Nmr spectra of the remaining aqueous solution indicated the presence of the $(\text{CF}_3)_2\text{PO}_2^-$ ³⁸ and $\text{CF}_3\text{PO}_3\text{H}^-$ ion in the ratio 6:1.

(d) With Dimethylamine

A sample of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.092 g, 0.28 mmoles) and $(\text{CH}_3)_2\text{NH}$ (0.214 g, 4.76 mmoles) did not react over a period of 84 hours at room temperature. Vacuum fractionation gave $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.080 g, 0.24 mmoles) and

$(\text{CH}_3)_2\text{NH}$ (0.215 g, 4.78 mmoles). The nmr spectra of the white solid which remained in the reaction vessel indicated that it was only unchanged, $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$, which is relatively involatile and therefore incompletely transferred with the volatile products.

(e) With Hydrogen Chloride

Reaction of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and HCl occurred only under conditions of a large excess pressure of HCl. No reaction took place when $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.100 g, 0.31 mmoles) was treated with HCl (0.048 g, 1.33 mmoles) for two days at room temperature. The reaction of excess hydrogen chloride (0.633 g, 17.3 mmoles) and $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.193 g, 0.59 mmoles) for 48 hours at room temperature gave $(\text{CF}_3)_3\text{PCl}_2$ (0.099 g, 0.32 mmoles) and a mixture (0.550 g) of HCl and very small amounts of at least two unidentified compounds (indicated by ir) which trapped at -196°C . Nmr spectra of CD_3CN solutions of the involatile white solid which remained in the reaction vessel indicated that it consisted of large amounts of $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$ and very small amounts of several unidentified CF_3P containing compounds. [$J = 114 \text{ Hz}$, $\phi_{\text{F}} = 65.7 \text{ ppm}$; $J = 168 \text{ Hz}$, $\phi_{\text{F}} = 64.3 \text{ ppm}$].

(f) With Chloroform

A sample of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.131 g, 0.40 mmoles) was allowed to react with CCl_3H (0.317 g, 2.65 mmoles) for

2½ hours at room temperature. Vacuum fractionation of the volatile products gave unreacted CCl_3H (0.264 g, 2.21 mmoles) and a mixture (0.031 g) of CF_3H and CF_3Cl in the ratio of 10.4:1 (by nmr). A CD_3CN solution of the unstable dark brown solid which remained in the reaction vessel gave nmr parameters (Table XIII) which were consistent with its formulation as $(\text{CF}_3)_2(\text{CCl}_3)\text{P}[\text{N}(\text{CH}_3)_2]_2$. A second reaction gave a mixture of CF_3H and CF_3Cl in the ratio of 4:1 (by nmr). A CD_3CN solution of the unstable involatile solid gave nmr parameters for two compounds which were consistent with their formulation as $(\text{CF}_3)_2(\text{CCl}_3)\text{P}[\text{N}(\text{CH}_3)_2]_2$ and $(\text{CF}_3)_2(\text{CCl}_2\text{H})\text{P}[\text{N}(\text{CH}_3)_2]_2$ (Table XIII).

(g) With Methanol

The reaction of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.134 g, 0.41 mmoles) with CH_3OH (0.027 g, 0.85 mmoles) for 10 minutes at room temperature gave $(\text{CH}_3)_2\text{NH}$ (0.006 g, 0.13 mmoles) and CF_3H (0.030 g, 0.43 mmoles) as the only volatile products. The white involatile liquid of low volatility which remained in the reaction tube was dissolved in CD_3CN and the solution gave nmr parameters indicating the presence of $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$ (vide infra) and two as yet unidentified CF_3P containing compounds ($\phi_{\text{F}} = 74.1$ ppm, $J = 94$ Hz; $\phi_{\text{F}} = 72.7$ ppm, $J = 97$ Hz).

(h) With Methyl Mercaptan

The compound $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.096 g, 0.30 mmoles)

and CH_3SH (0.028 g, 0.58 mmoles) were allowed to react in a sealed tube at room temperature. Fractionation of the volatile products after 48 hours at room temperature gave an unseparated mixture (0.084 g) trapped at -116°C consisting of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ ³⁹ (0.039 g, 0.21 mmoles), $(\text{CF}_3)_2\text{PSCH}_3$ ⁴⁰ (0.010 g, 0.05 mmoles), $(\text{CF}_3)_3\text{P}$ ²⁰ (0.003 g, 0.01 mmoles) and CH_3SSCH_3 ⁴¹ (0.032 g, 0.34 mmoles) together with a small amount of $(\text{CH}_3)_2\text{NH}$ (as determined by nmr spectroscopy). CF_3H (0.035 g, 0.50 mmoles) was collected in the -196°C trap.

(i) With Hydrogen Sulphide

The reaction of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.252 g, 0.77 mmoles) and H_2S (0.053 g, 1.56 mmoles) proceeded rapidly and exothermally at room temperature. After 10 minutes the reaction subsided and subsequent vacuum fractionation afforded $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$ ⁴² (0.020 g, 0.09 mmoles) (vide infra) $(\text{CF}_3)_2\text{P}(\text{S})\text{N}(\text{CH}_3)_2$ ⁴³ (0.025 g, 0.10 mmoles), $(\text{CH}_3)_2\text{NH}$ (0.012 g, 0.27 mmoles) and CF_3H (0.056 g, 0.80 mmoles) which was purified by washing with a degassed solution of lead acetate to remove any traces of H_2S . The nmr spectra of the involatile liquid which remained in the reaction tube after fractionation indicated the presence of the $(\text{CF}_3)_2\text{PS}_2^-$ ions. ³⁸

3. Preparation and Characterization of Tris(trifluoromethyl)chlorodimethylaminophosphorane

(a) Preparation from $(\text{CF}_3)_3\text{PCl}_2$ and $(\text{CH}_3)_2\text{NH}$

Using the apparatus shown in Figure 1 tris(trifluoromethyl)dichlorophosphorane $(\text{CF}_3)_3\text{PCl}_2$ ²⁰ (0.757 g, 2.45 mmoles) and gaseous $(\text{CH}_3)_2\text{NH}$ (0.227 g, 5.04 mmoles) were allowed to react for only 5 minutes at room temperature. Vacuum fractionation gave a mixture (0.528 g) which was collected at -45°C containing $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ (0.401 g, 1.26 mmoles) and $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.127 g, 0.39 mmoles) (analyzed by nmr spectroscopy). Pure $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ was obtained by further careful fractionation of the -45°C mixture. $(\text{CF}_3)_3\text{PCl}_2$ (0.198 g, 0.64 mmoles) was found in the -96°C trap and unreacted $(\text{CH}_3)_2\text{NH}$ (0.456 g, 1.01 mmoles) was collected in the -196°C trap.

(b) Characterization of $(\text{CF}_3)_3\text{PCl}[\text{N}(\text{CH}_3)_2]$

The compound is a white solid which decomposes quite rapidly over a period of days at room temperature. The decomposition of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ in a CFCl_3 solution was followed by nmr spectroscopy over a period of 48 hours at room temperature. A small amount of $(\text{CF}_3)_3\text{P}$ was the only identifiable CF_3P containing decomposition product.

The compound was characterized by its spectroscopic properties (ir Table II, nmr Table XIII) by mass spectrometry (Table IV) and by chemical reactions described below.

TABLE IV

Mass Spectrum of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$

<u>m/e</u>	<u>rel. int.^a</u>	<u>assignment</u>	<u>m/e</u>	<u>rel. int.^a</u>	<u>assignment</u>
282 ^b	1.4	$\text{C}_5\text{F}_9\text{H}_6\text{NP}$	100	3.8	CF_3P
275	0.1	$\text{C}_3\text{F}_9\text{ClP}$	97	1.0	$\text{CF}_2\text{H}_2\text{NP}$
273	0.4		94	10.2	$\text{C}_2\text{FH}_6\text{NP}$
250	0.3	$\text{C}_4\text{F}_6\text{ClH}_6\text{NP}$	90	1.1	$\text{C}_2\text{FH}_2\text{NP}$
248 ^b	1.1		81	1.0	C_2F_3
232	3.8	$\text{C}_4\text{F}_7\text{H}_6\text{NP}$	69	12.2	CF_3
229	1.7	$\text{C}_4\text{F}_7\text{H}_3\text{NP}$	60	1.3	CH_3NP
207	0.8	C_3F_9	51	3.1	CF_2H
182	3.1	$\text{C}_3\text{F}_5\text{H}_6\text{NP}$	50	2.4	CF_2
166	0.9	$\text{C}_4\text{F}_6\text{H}_4$	47	9.8	H_2NP
160	3.8	$\text{C}_3\text{F}_4\text{H}_3\text{NP}$	44	2.4	$\text{C}_2\text{H}_6\text{N}$
150	1.0	$\text{C}_2\text{F}_5\text{P}$	43	2.6	$\text{C}_2\text{H}_5\text{N}$
135	1.3	$\text{CF}_4\text{H}_2\text{NP}$	42	7.5	$\text{C}_2\text{H}_4\text{N}$
132	3.7	$\text{C}_2\text{F}_3\text{H}_6\text{NP}$	31	5.8	CF
128	0.7	$\text{C}_2\text{F}_3\text{H}_2\text{NP}$			
119	6.2	CF_4P			
110	5.5	$\text{C}_2\text{F}_2\text{H}_3\text{NP}$			

(a) Intensities are expressed relative to the total ionization defined as $\sum_n (\text{intensity})$ for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak.

(continued.....)

Footnotes to Table IV (continued)

(b) The identity of these peaks was established by mass measurement under high resolution.

Ion	m/e calc.	m/e obs
$\text{C}_5\text{F}_9\text{H}_6\text{NP}^+$	282.0093	282.0086
$\text{C}_4\text{F}_6^{35}\text{ClH}_6\text{NP}^+$	247.9830	247.9824

4. Reactions of Tris(trifluoromethyl)chlorodimethylamino-phosphorane.

(a) Neutral Hydrolysis

Reaction of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ (0.223 g, 0.70 mmoles) with approximately 0.8 mls of degassed distilled H_2O at room temperature for 48 hours gave CF_3H (0.049 g, 0.70 mmoles). Nmr spectra of the remaining aqueous solution showed the presence of the $(\text{CF}_3)_2\text{PO}_2^-$ ion.³⁸

(b) Alkaline Hydrolysis

Hydrolysis of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ (0.069 g, 0.22 mmoles) with approximately 0.8 mls of degassed 10% NaOH at room temperature for 24 hours gave CF_3H (0.029 g, 0.42 mmoles). Nmr spectra of the remaining aqueous solution showed the presence of the $\text{CF}_3\text{PO}_3^{=}$ ion.³⁸

(c) Acid Hydrolysis

The compound $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ (0.124 g, 0.39 mmoles) was allowed to react with 0.8 mls of degassed distilled water adjusted to a $\text{pH} \approx 1$ by the addition of HCl. After 24 hours at room temperature vacuum fractionation afforded CF_3H (0.028 g, 0.40 mmoles). Nmr spectra of the remaining aqueous solution indicated the presence of the $(\text{CF}_3)_2\text{PO}_2^-$ ion.³⁸

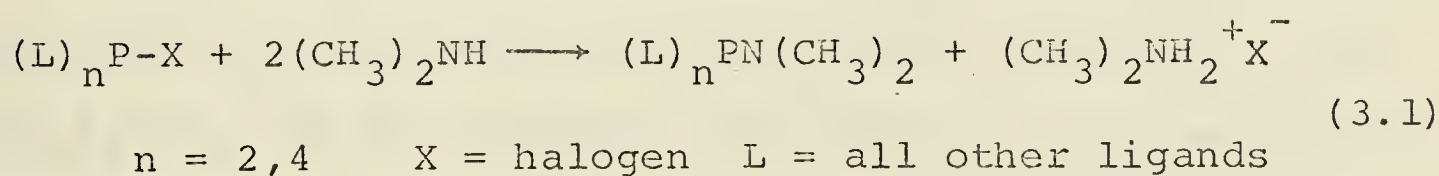
(d) With Dimethylamine

The reaction of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ (0.133 g, 0.42

mmoles) with $(\text{CH}_3)_2\text{NH}$ (0.107 g, 2.38 mmoles) at room temperature for 24 hours gave $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.130 g, 0.40 mmoles) which was trapped at -63°C and unreacted $(\text{CH}_3)_2\text{NH}$ (0.073 g, 1.62 mmoles) which was trapped at -116°C . The white solid which remained in the reaction tube was identified as the $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$ salt by nmr.

5. Results and Discussion

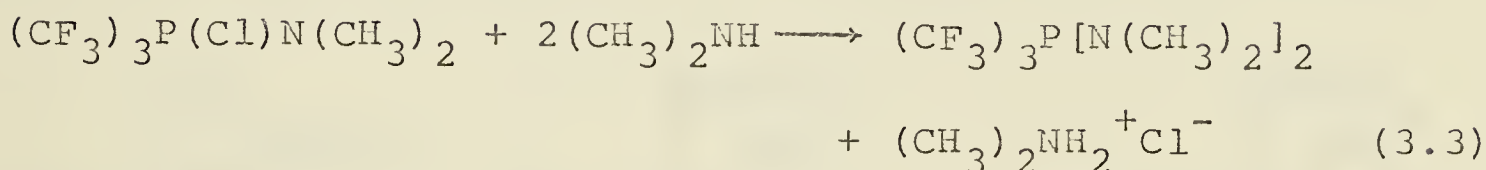
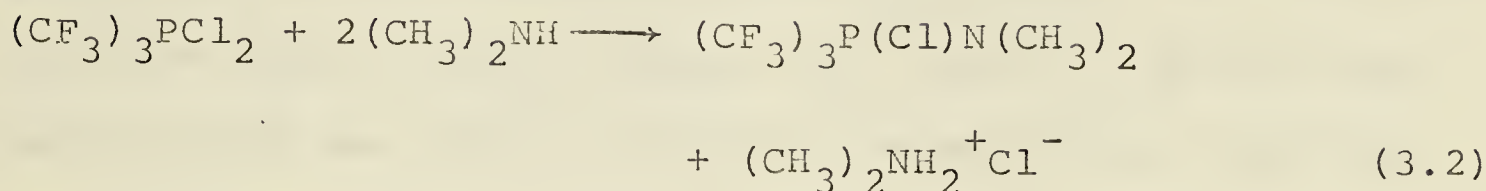
A reaction which is characteristic of halogen containing phosphorus compounds (both tri- and pentavalent) is the replacement of the halogen substituent by a dimethylamino group upon reaction with $(\text{CH}_3)_2\text{NH}$ according to eqn (3.1).



The attack by nucleophiles such as $(\text{CH}_3)_2\text{NH}$ on the P atom is facilitated by the high electronegativity of the trifluoromethyl group. Among the typical trifluoromethyl derivatives prepared in this manner are $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ ³⁹, $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ ³⁶, $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$ ⁴², $\text{CF}_3(\text{F})\text{PN}(\text{CH}_3)_2$ ³⁹ and $(\text{CF}_3)_2\text{P}(\text{S})\text{N}(\text{CH}_3)_2$ ⁴².

Extending this series of reactions to a pentacoordinated system, we found that the reaction of $(\text{CF}_3)_3\text{PCl}_2$ and $(\text{CH}_3)_2\text{NH}$ proceeded very smoothly in a stepwise process leading to the isolation of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ and

$(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ according to eqns (3.2, 3.3).

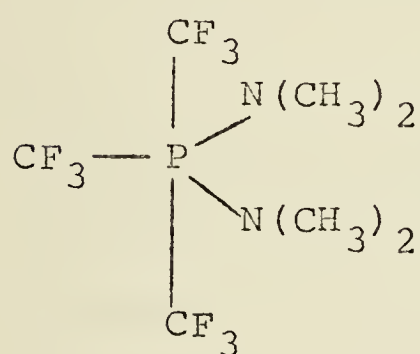


The reaction of $(\text{CF}_3)_3\text{PCl}_2$ and 2 moles of $(\text{CH}_3)_2\text{NH}$ gave a 51% conversion to $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$, 16% conversion to $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and 26% of $(\text{CF}_3)_3\text{PCl}_2$. The conversion to $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and recovery of $(\text{CF}_3)_3\text{PCl}_2$ could possibly be explained by either preferential attack of $(\text{CH}_3)_2\text{NH}$ on the P-Cl bond of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ rather than that of $(\text{CF}_3)_3\text{PCl}_2$ or by a surface phenomenon since $(\text{CF}_3)_3\text{PCl}_2$ and the products are solids at room temperature. The properties and characterization of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ are described on page 20.

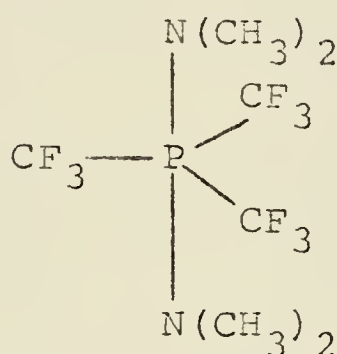
When four molar equivalents of $(\text{CH}_3)_2\text{NH}$ were reacted with $(\text{CF}_3)_3\text{PCl}_2$ the compound $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ was obtained in 89% yield. This compound was also produced from the reaction of the intermediate $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ with two moles of $(\text{CH}_3)_2\text{NH}$.

According to Muetterties and Schunn¹⁰, the most likely geometry for a pentavalent, pentacoordinated phosphorus atom is a trigonal bipyramidal model as shown below. The possible arrangements of CF_3 and $\text{N}(\text{CH}_3)_2$

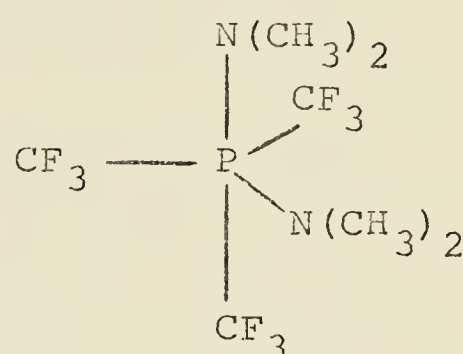
groups within the compound $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ are (1) a structure with two equatorial $\text{N}(\text{CH}_3)_2$ groups (I), (2) one with two axial $\text{N}(\text{CH}_3)_2$ groups (II) and (3) a third alternative with one $\text{N}(\text{CH}_3)_2$ group in the equatorial position and the other $\text{N}(\text{CH}_3)_2$ group in the axial position (III).



I



II



III

The room temperature ^1H nmr spectrum shows an apparent doublet of either octets or decets (Figure 3) with an intensity distribution in good agreement with that expected for the central eight lines of a ten line pattern. This spectrum arises from coupling to a phosphorus nucleus and nine equivalent fluorine atoms thus confirming the presence of three CF_3 groups on phosphorus. On cooling the sample to -80°C the doublet observed in the ^1H spectrum remained unchanged indicating that the $\text{N}(\text{CH}_3)_2$ groups are equivalent at this temperature suggesting that structure (III) probably does not occur although it cannot be conclusively excluded by this evidence.

At room temperature the ^{19}F nmr spectrum was a

FIGURE 3

The upper portion of the figure shows the calculated (stick diagram) and observed (lower trace) 100 MHz ^1H nmr spectra of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ obtained at 40°C . The frequency scale is measured relative to TMS with positive sign denoting lower field.

The lower portion of the figure shows the calculated (stick diagram) and observed 94.1 MHz ^{19}F nmr spectra of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ at -40°C . The frequency scale is measured relative to CFCl_3 with positive sign denoting high field.

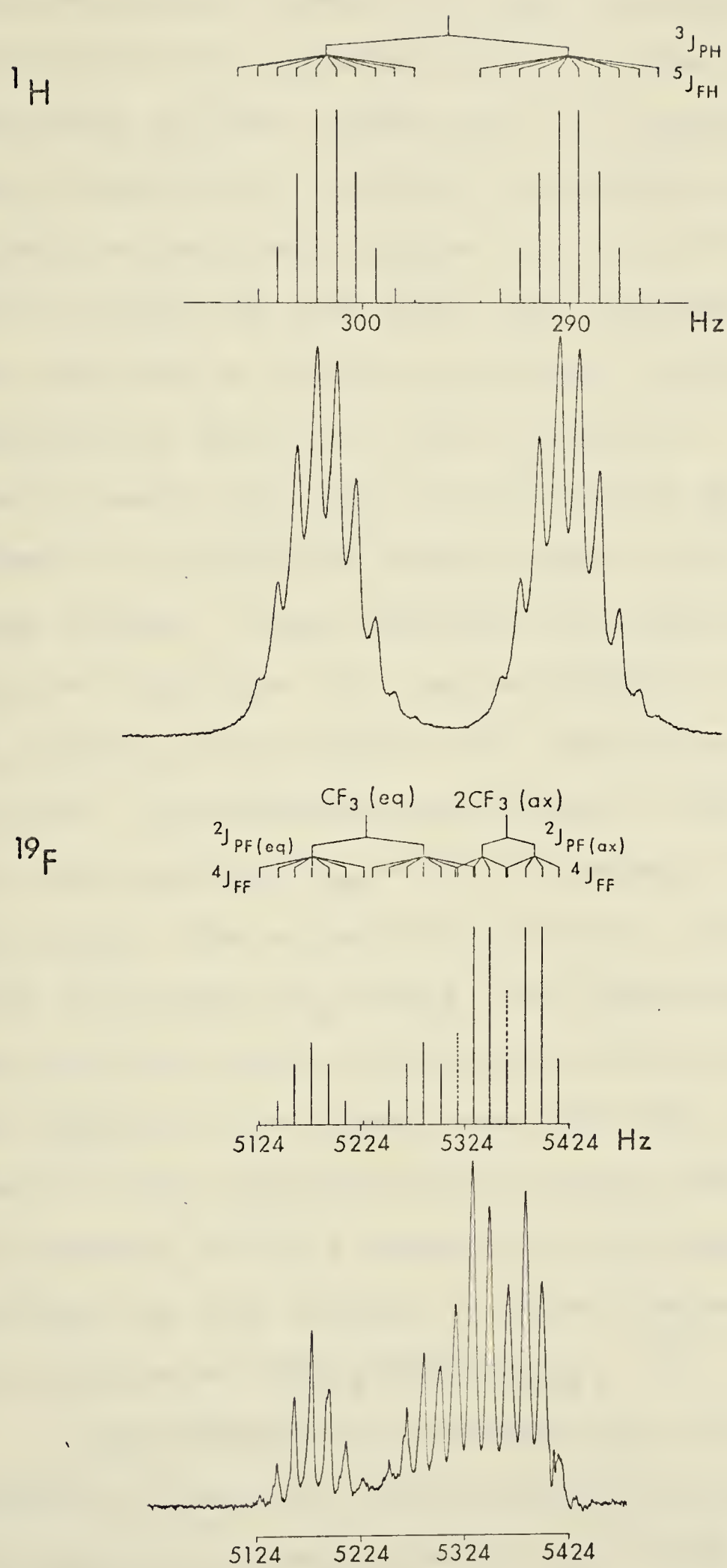


FIGURE 3. The ^1H and ^{19}F nmr spectra of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$

broad multiplet (Figure 4). Upon cooling to -30°C the multiplets were completely resolved into two overlapping chemically shifted regions with 2:1 intensity ratio. These consisted of a doublet of quartets and a doublet of septets respectively (Figure 4). At -90°C the higher intensity peaks had lost their fine structure (Figure 4) and were replaced by further unresolved complex multiplets appearing in detail at -140°C (Figure 4). The lower intensity peaks lost their fine structure at -115°C (Figure 4) and did not resolve again within the temperature range studied. These features are understandable on the basis of structure (I), the two different environments of CF_3 groups giving rise to well resolved multiplets observed at -30°C . The quartets and septets in this spectrum result from the coupling $^4J_{\text{FF}} = 16.5 \text{ Hz}$ between the two types of CF_3 groups, thus eliminating structure (II) which contains three equivalent CF_3 groups. At temperatures below -90°C the rotational motion of the CF_3 groups about the P-C bond axis appears to be slowed down such that a complex 2nd order ^{19}F nmr spectrum results because the different environments of the F atoms can be distinguished. These features are very similar to those observed in the ^{19}F nmr spectrum of $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$.³³

The proposal of structure (I) as the preferred structure agrees with that predicted on the basis of the proposal by Muetterties et al¹¹ that the more

FIGURE 4

Temperature dependence of the ^{19}F nmr spectrum of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$. The spectrum obtained at 75° was measured at 56.4 MHz on a C_6F_6 solution of the compound while those obtained at 27° , -30° , -90° , -115° and -140°C were measured at 84.7 MHz on a CF_2Cl_2 solution of the compound. The frequency scales are measured relative to CFCl_3 with positive sign denoting resonance to high field of the standard.

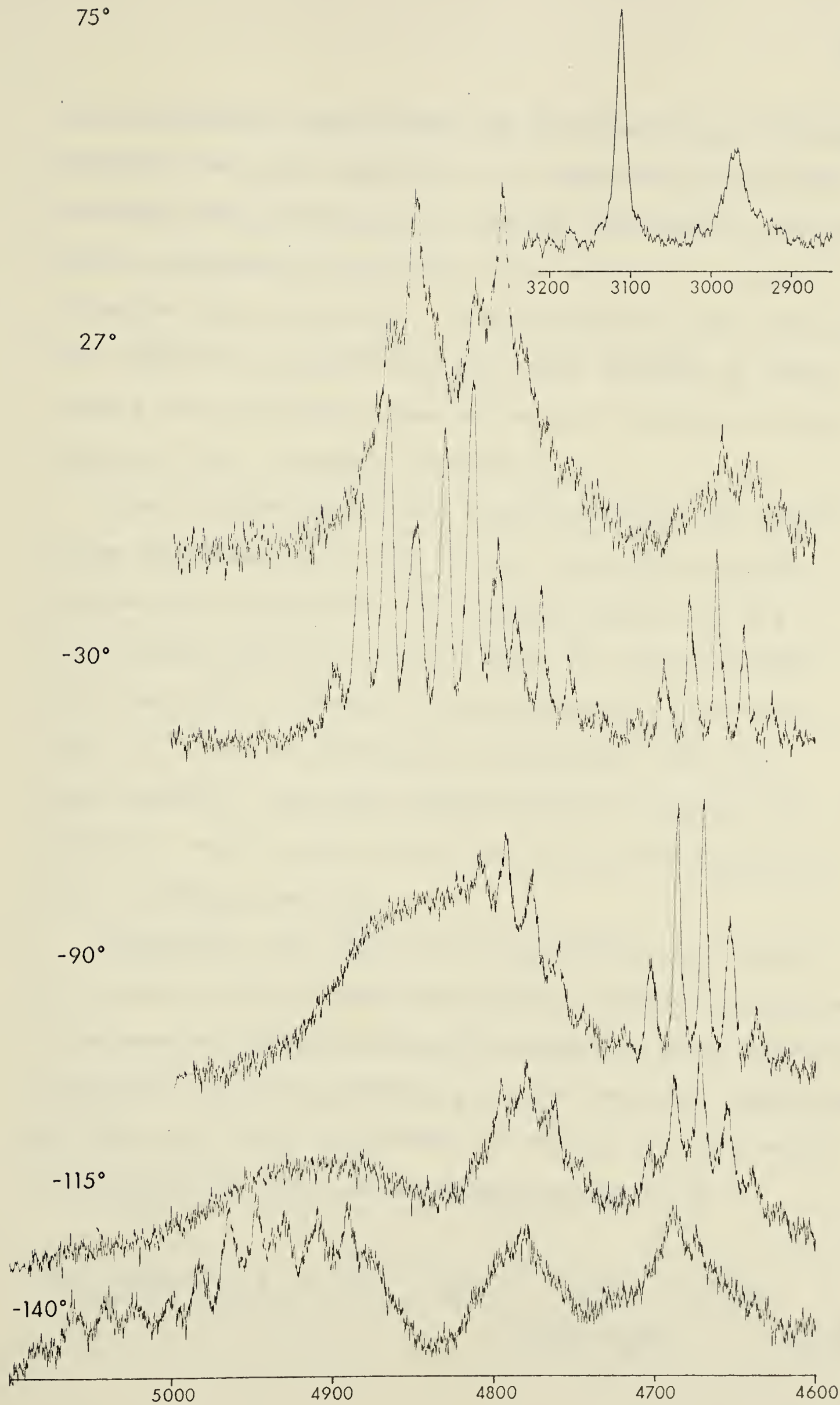
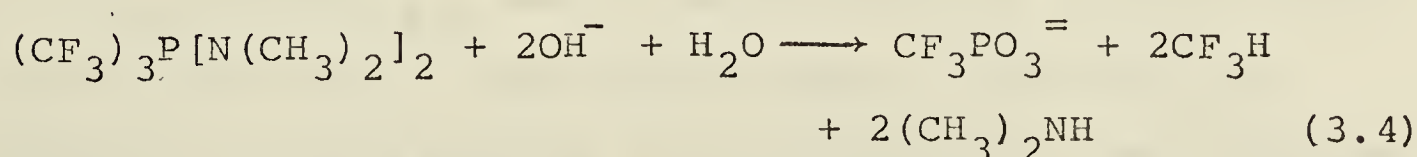


FIGURE 4. Temperature Dependence of the ^{19}F nmr Spectra of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$

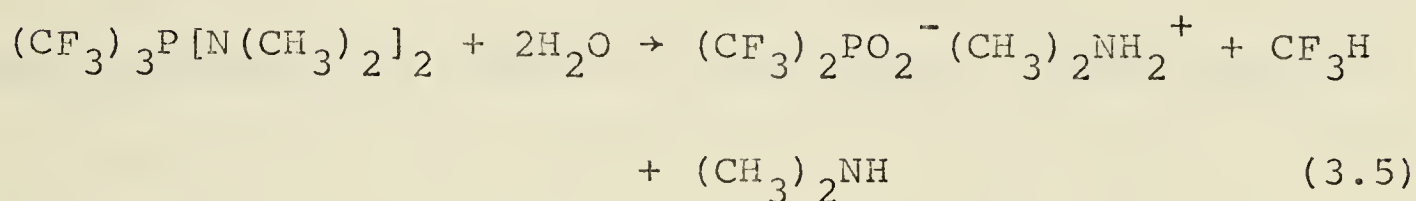
electronegative substituent (in this case CF_3) uniformly occupies the axial position. At relatively high temperatures the distinction is usually obscured by environmental averaging of the substituents due to a pseudo-rotation type of process. Such a process also occurs in the compound $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ since heating to $+75^\circ\text{C}$ caused the multiplets observed at room temperature to coalesce into a doublet (Figure 4).

The ir spectrum is also consistent with the formulation described above but did not allow distinction between the structures. The expected peaks for CF_3 substituents and CH_3 groups (Table II) were observed and also peaks assigned as asymmetric N_2P stretch (660 cm^{-1}) and an asymmetric C_2N stretch (987 cm^{-1}) were present. The mass spectrum gave two peaks (m/e 282, 257) which could arise from $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ by loss of $\text{N}(\text{CH}_3)_2$ and CF_3 .

Chemically the compound $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ behaves as a tris(trifluoromethyl)phosphorus compound containing a pentavalent pentacoordinated phosphorus atom. Alkaline hydrolysis of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ gave two molar equivalents of CF_3H , one molar equivalent of $\text{CF}_3\text{PO}_3^{=}$ and two molar equivalents of $(\text{CH}_3)_2\text{NH}$ according to eqn (3.4).



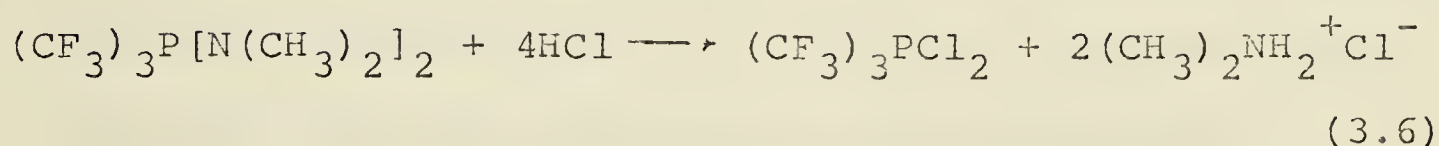
In neutral aqueous solution a yield of one molar equivalent of CF_3H , one molar equivalent of $(\text{CF}_3)_2\text{PO}_2^-$ ³⁸ and two molar equivalents of $(\text{CH}_3)_2\text{NH}$ according to eqn (3.5) would be expected.^{44,45}



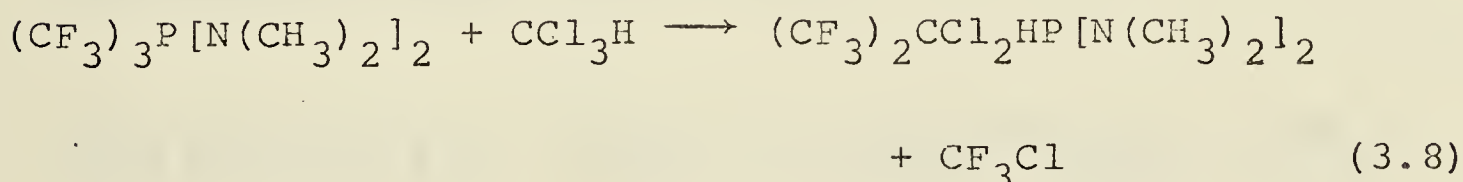
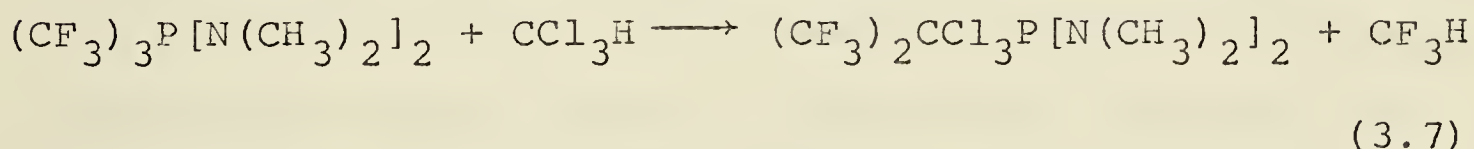
Instead 1.4 molar equivalents of CF_3H were obtained and this excess CF_3H was shown to arise from the localized base reaction of the leaving $(\text{CH}_3)_2\text{NH}$ groups, since the hydrolysis in strongly acidic medium ($\text{pH} \approx 1$) gave 1.05 molar equivalents of CF_3H , 0.86 molar equivalents of $(\text{CF}_3)_2\text{PO}_2^-$ and 0.14 molar equivalents of $\text{CF}_3\text{PO}_3\text{H}^-$. This localized effect of the leaving $(\text{CH}_3)_2\text{NH}$ groups thus occurs to a small extent even in acidic solutions as demonstrated by the evolution of slightly more than one molar equivalent of CF_3H and formation of the new singly protonated monotrifluoromethyl phosphorus anion $\text{CF}_3\text{PO}_3\text{H}^-$. This species was characterized by comparing its nmr parameters with the known³⁸ related species $\text{CF}_3\text{PS}_2\text{OH}^-$, $\text{CF}_3\text{PSO}_2\text{H}^-$ and by conversion to the known anion CF_3PO_3^- in basic solution.

Starting materials were recovered from the reaction of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and a large excess of $(\text{CH}_3)_2\text{NH}$ over a period of days at room temperature. Similarly no reaction occurred between $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and anhydrous

HCl at low pressures. However $(\text{CF}_3)_3\text{PCl}_2$ was obtained in 54.3% yield when $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ was allowed to react with a large excess pressure of HCl according to eqn (3.6).



The reaction of excess chloroform and $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ occurred with the consumption of one molar equivalent of chloroform. The only volatiles recovered were unreacted CCl_3H and a mixture of mainly CF_3H and smaller amounts CF_3Cl in yields consistent with the stoichiometries described by eqns (3.7, 3.8).



The involatile residue from the reaction had the appearance of a brown oil. Nmr spectra of this oil dissolved in CD_3CN gave signals which could be interpreted as arising from products $(\text{CF}_3)_2\text{CCl}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and $(\text{CF}_3)_2\text{CCl}_2\text{HP}[\text{N}(\text{CH}_3)_2]_2$. Further characterization of the phosphoranes was not attempted owing to their apparent thermal instability and the difficulty in handling involatile

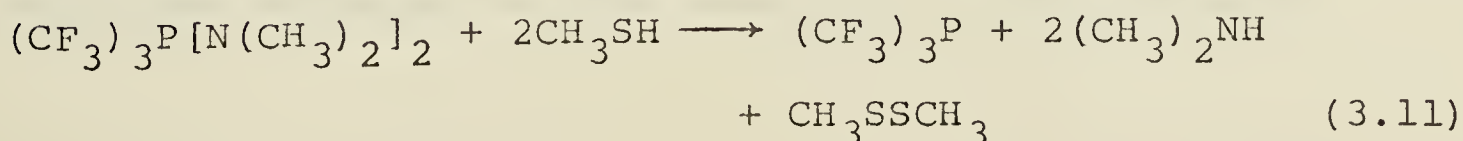
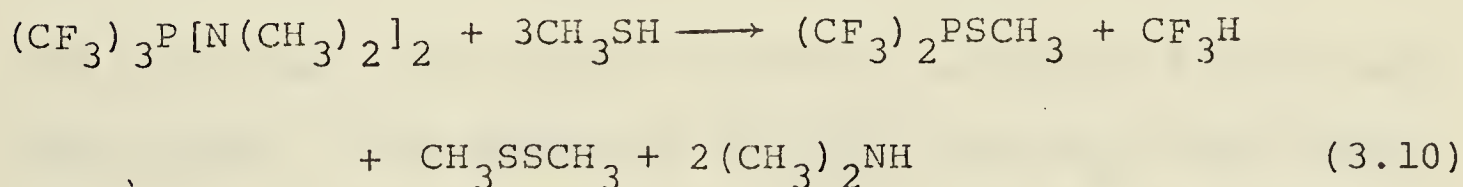
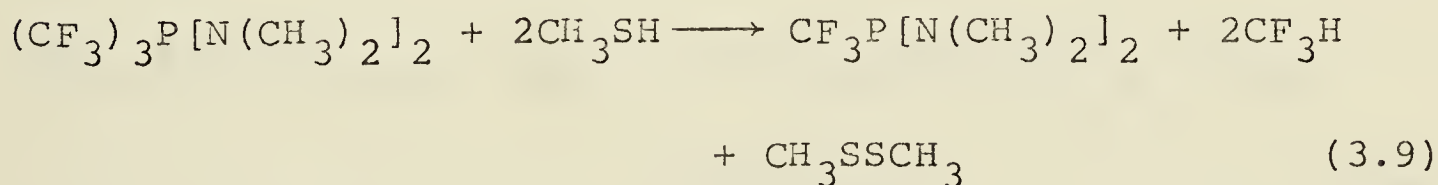
substances.

The only identified phosphorus containing product resulting from the reaction of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and CH_3OH was $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$. CF_3H was also found among the products. In addition smaller amounts of at least two other unidentified CF_3P containing compounds were detected among the products by nmr spectroscopy.

($\phi_{\text{F}} = 74.1$ ppm, $J = 94$ Hz; $\phi_{\text{F}} = 72.7$ ppm, $J = 97$ Hz).

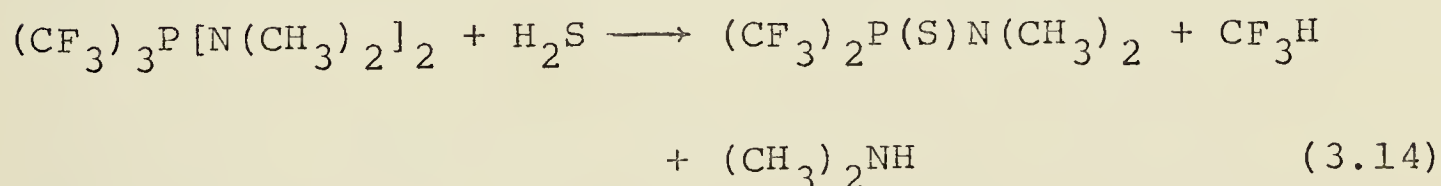
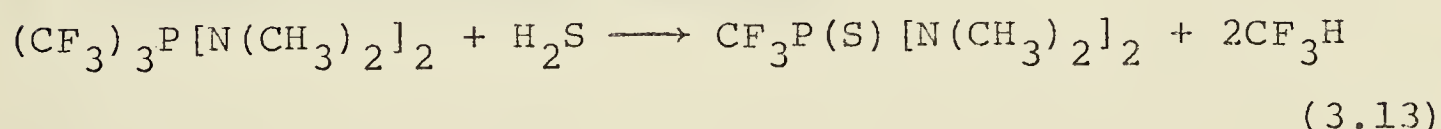
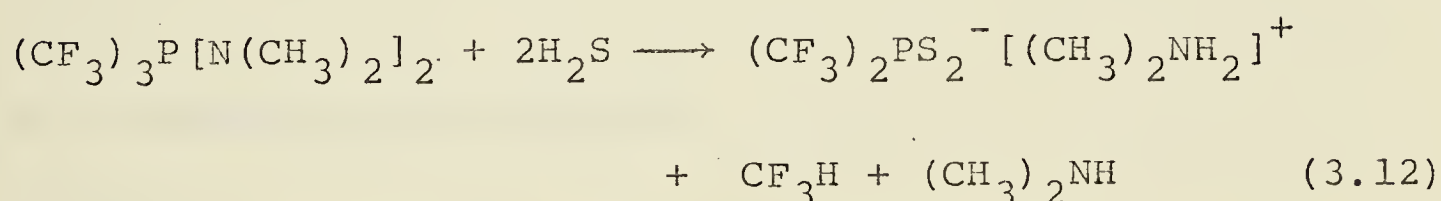
The previously unknown $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$ was identified by comparison with a sample whose preparation and characterization are described in Chapter 6.

The reaction of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ with CH_3SH appeared to proceed along three pathways leading to $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$, $(\text{CF}_3)_2\text{PSCH}_3$ and $(\text{CF}_3)_3\text{P}$ as the major phosphorus containing products in 68.5%, 15.5% and 4.5% yield respectively. Simplified routes leading to these three compounds are represented in eqns (3.9 - 3.11)



although the overall reaction mechanism is quite possibly more complicated. Other products identified were CF_3H , CH_3SSCH_3 and $(\text{CH}_3)_2\text{NH}$ produced in amounts consistent with the above stoichiometries (Table V). The yield of unique P compound was used to estimate the contribution of each reaction to the total.

Treatment of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ with H_2S gave a 11.7% and 13.0% yields of $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$ ⁴² and $(\text{CF}_3)_2\text{P}(\text{S})\text{N}(\text{CH}_3)_2$ ⁴² respectively and a 67.5% yield of $(\text{CF}_3)_2\text{PS}_2^-$ ³⁸ ion as deduced from the amount of CF_3H evolved. These results can be summarized by the eqns (3.12 - 3.14)



although again the overall reaction mechanism may be more complicated. The yields of $(\text{CH}_3)_2\text{NH}$ and CF_3H were again consistent with the stoichiometries described by these equations allowing for the reaction of $(\text{CH}_3)_2\text{NH}$ with

TABLE V

Reaction Products of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ and CH_3SH

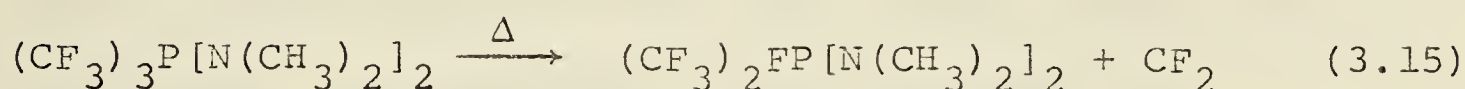
	<u>eq</u> <u>(3.9)</u>	<u>eq</u> <u>(3.10)</u>	<u>eq</u> <u>(3.11)</u>	<u>calc</u>	<u>obs</u>
CF_3H	0.42	0.05	-	0.47	0.50
CH_3SSCH_3	0.21	0.05	0.01	0.27	0.34 ^a
$(\text{CH}_3)_2\text{NH}$	-	0.10	0.02	0.12	b

a . contains some $(\text{CH}_3)_2\text{NH}$ b Present in CH_3SSCH_3 fraction

excess H_2S . The product $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$ which had been previously prepared⁴² but no nmr spectra reported, was identified by comparison with a sample whose preparation and characterization are described in Chapter 6.

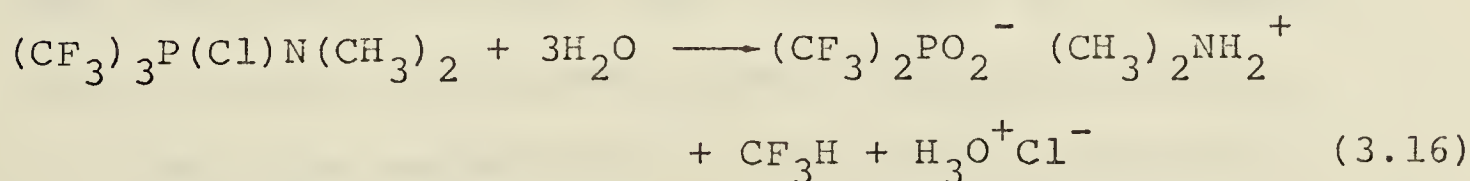
The compound $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ was found to decompose thermally at 100°C yielding initially

$(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$, $(\text{CF}_2)_3$ and $(\text{CF}_2)_2$ according to eqn (3.15)

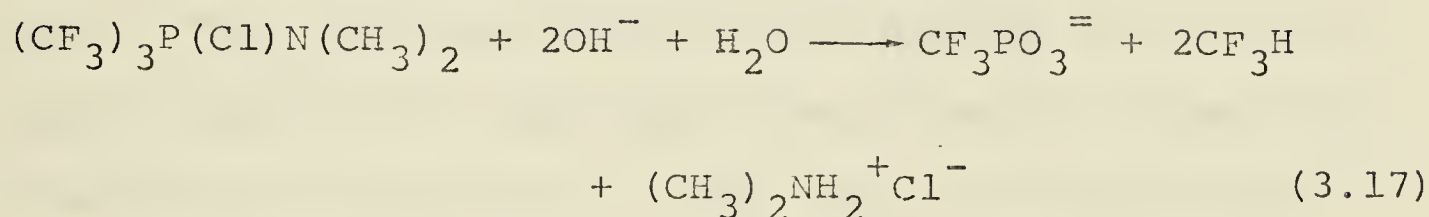


followed by dimerization and trimerization of the CF_2 radical. This reaction thus provides a further proof of the formulation $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$. Further studies of the thermal decomposition products are described in Chapter 4.

The instability of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ at room temperature made the chemical characterization of this compound rather difficult. As a result, only a few reactions were investigated. Reaction with excess dimethylamine removed the Cl atom and gave rise to $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$. Acidic and neutral hydrolysis of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ each gave one molar equivalent of CF_3H according to the eqn (3.16).



The basic hydrolysis resulted in the formation of two molar equivalents of CF_3H according to the eqn (3.17).



The above results are in complete agreement with the predicted behavior of pentacoordinate pentavalent phosphorus systems which do not form a basic medium upon hydrolysis. As described in the hydrolysis of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$, this basic medium resulted in the formation of more than one mole of CF_3H under "neutral" hydrolysis conditions. In the present case, hydrolysis of the chloride moiety would result in an acidic rather than a basic medium, and only one mole of CF_3H should be evolved, as was observed.

The ir spectrum which gave the expected absorptions for the CF_3 and the CH_3 groups, also gave peaks at 988 cm^{-1} , 593 cm^{-1} and 578 cm^{-1} which can be interpreted as arising from asymmetric C_2N stretching, asymmetric N_2P stretching and P-Cl stretching vibrations. The mass spectrum gave two peaks which were shown by accurate mass measurements to be the $\text{C}_5\text{F}_9\text{H}_6\text{NP}^+$ and $\text{C}_4\text{F}_6\text{H}_6\text{NP}^{35}\text{Cl}^+$ ions resulting from the loss of Cl and CF_3 respectively from the unobserved parent $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$.

The room temperature ^1H nmr spectrum shows an

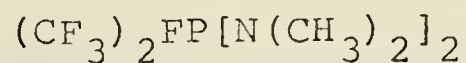
apparent doublet of either octets or decets, with an intensity distribution in good agreement with that expected for the central eight lines of a ten line pattern. This spectrum arises from coupling to the phosphorus nucleus and nine equivalent fluorine atoms thus confirming the presence of the three trifluoromethyl groups on phosphorus. The ^{19}F nmr spectrum showed a doublet of septets arising from coupling to the phosphorus nucleus and six equivalent hydrogen atoms, thus confirming the presence of a single dimethylamine group. Low temperature ^{19}F nmr studies were carried out for this compound in an attempt to determine its stereochemistry in a manner analogous to the study of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$. Preliminary experiments showed that the two compounds behaved similarly, with the two CF_3 groups being partially resolved into two chemically shifted regions as described on page 28. However, these features are partially resolved in $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ only at -120°C (the lowest operating temperature available) whereas in $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ these same features were present at room temperature, Figure 4. As a result reliable conclusions regarding the stereochemistry of $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ could not be obtained.

CHAPTER IV

THE PYROLYSIS OF TRIS(TRIFLUOROMETHYL) BIS(DIMETHYLAMINO)-PHOSPHORANE $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$

The fluorophosphoranes $(\text{CF}_3)_3\text{PF}_2$ ²⁶, $(\text{CF}_3)_2\text{PF}_3$ ²⁶ and CF_3PF_4 ²⁶ decompose at ordinary temperatures by elimination of the CF_2 radical and form a series which leads ultimately to PF_5 . The only other trifluoromethylphosphorane whose thermal decomposition has been studied is $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ which appeared to decompose by two major routes, the first leading to $(\text{CF}_3)_2\text{P}(\text{O})\text{OSi}(\text{CH}_3)_3$, $(\text{CF}_3)_3\text{SiF}$ and CF_2 radicals (the latter two presumably arising from decomposition of the unknown $(\text{CH}_3)_3\text{SiCF}_3$) and the second giving $(\text{CF}_3)_3\text{PO}$ and $[(\text{CH}_3)_3\text{Si}]_2\text{O}$. We report herein the synthesis and some chemical and physical properties of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ and $\text{CF}_3\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ which arise from the thermal decomposition of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ by successive difluorocarbene eliminations.

1. Preparation and Characterization of Bis(trifluoromethyl)bis(dimethylamino)fluorophosphorane.



(a) Preparation from $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$

$(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.520 g, 1.59 mmoles) was heated for 2½ hours at 100°C. Vacuum fractionation gave the new phosphorane $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ (0.329 g, 1.19 mmoles) in a 75% yield which was collected at -45°C. Analysis of the

mixture (0.071 g) trapping at -196°C showed the presence of $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$, $(\text{CF}_3)_3\text{P}$, CF_3H , $(\text{CF}_2)_3$ ($\phi_{\text{F}} = 158.8$ ppm, lit.⁴⁶ for neat liquid 160.9 ppm) and $(\text{CF}_2)_2$ ($\phi_{\text{F}} = 134.1$ ppm, lit.⁴⁷ 134.6 ppm as a 10% solution in CFCl_3) in the molar ratio 1 : 1.6 : 8.0 : 21 : 44 (by nmr spectroscopy). Thus the overall yield of $(\text{CF}_2)_n$ was 0.062 g (1.24 mmole " CF_2 ", 78%). The nmr spectra of the brown involatile oil which remained in the reaction vessel showed that it contained a trace of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ and an unidentified product containing the $\text{CF}_3\text{PN}(\text{CH}_3)_2$ grouping with the following nmr parameters ($\phi_{\text{F}} = 60.8$ ppm, $^2J_{\text{PF}} = 116$ Hz, $\tau = 6.95$, $^3J_{\text{PH}} = 11.4$ Hz).

(b) Physical Properties

The compound is a colourless solid melting at 15°C . It is stable over a period of months at room temperature. $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ was characterized by its spectroscopic properties (ir Table VI, nmr Table XIII) by mass spectroscopy (Table VII) and by the chemical reactions described below.

(c) Alkaline Hydrolysis of the Monofluorophosphorane

Hydrolysis of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ (0.118 g, 0.43 mmols) with 0.5 mls of degassed 10% NaOH solution for 24 hours at room temperature gave CF_3H (0.033 g, 0.47 mmols). The ^{19}F nmr spectrum of the remaining aqueous solution indicated the presence of the $\text{CF}_3\text{PO}_3^{=}$ ion.³⁸

TABLE VI

Infrared Spectra of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ and $(\text{CF}_3)_2\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$

$(\text{CF}_3)_2\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$	$(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$	Assignment
3042 (vw, sh)	3040 (vw, sh)	} $\nu(\text{C-H})$
2952 (m)	3010 (vw)	
2923 (w, sh)	2943 (m)	
2880 (w)	2920 (w, sh)	
2830 (w)	2879 (w)	
	2830 (w)	
1470 (w)	1467 (w)	} $\delta(\text{CH}_3), \nu_s(\text{C}_2\text{-N})$
1297 (m)	1290 (m)	
1217 (s)	1224 (m, sh)	} $\nu(\text{C-F})$
1176 (vs)	1195 (vs)	
1131 (vs)	1154 (vs)	
	1135 (vs)	
1070 (w)	1085 (m)	} $\nu_{as}(\text{C}_2\text{-N})$
1023 (vs)	1004 (m)	
896 (vs)	830 (vs)	} $\nu(\text{P-F})$
810 (s)	755 (m)	
771 (s)		

(continued.....)

TABLE VI (continued)

<u>$(\text{CF}_3)_2\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$</u>	<u>$(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$</u>	<u>Assignment</u>
	727 (w)	$\nu_{\text{as}}(\text{CF}_3)$
673 (s)	678 (m)	$\nu_{\text{as}}(\text{N}_2\text{-P})$
	662 (m)	
609 (w)	609 (vw)	$\nu_{\text{as}}(\text{CF}_3)$
541 (m)		

(a) All values in cm^{-1}

(b) Abbreviations: ν = stretching, δ = deformation,
 s = strong, m = medium, w = weak, v = very,
 sh = shoulder, as = antisymmetric, s = symmetric.

TABLE VII

Mass Spectra of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ and $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$

$(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$			$(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$		
m/e	Rel. int. ^a	Assignment	m/e	Rel. int. ^a	Assignment
257 ^b	0.5	$\text{C}_6\text{F}_6\text{H}_{12}\text{N}_2\text{P}$	226 ^c	0.7	$\text{C}_5\text{F}_5\text{H}_{12}\text{N}_2\text{P}$
238	1.2	$\text{C}_6\text{F}_5\text{H}_{12}\text{N}_2\text{P}$	207 ^c	0.5	$\text{C}_5\text{F}_4\text{H}_{12}\text{N}_2\text{P}$
232 ^b	9.5	$\text{C}_4\text{F}_7\text{H}_6\text{NP}$	182 ^c	9.9	$\text{C}_3\text{F}_5\text{H}_6\text{NP}$
207	1.2	$\text{C}_5\text{F}_4\text{H}_{12}\text{N}_2\text{P}$	157	4.4	$\text{C}_4\text{F}_2\text{H}_{12}\text{N}_2\text{P}$
195	1.4	$\text{C}_4\text{F}_5\text{H}_7\text{NP}$	153	1.1	$\text{C}_4\text{F}_2\text{H}_8\text{N}_2\text{P}$
194	26.4	$\text{C}_4\text{F}_5\text{H}_6\text{NP}$	151	1.7	$\text{C}_4\text{F}_2\text{H}_6\text{N}_2\text{P}$
182	7.4	$\text{C}_3\text{F}_5\text{H}_6\text{NP}$	137	0.6	$\text{C}_4\text{FH}_{11}\text{N}_2\text{P}$
178	1.1	$\text{C}_3\text{F}_5\text{H}_2\text{NP}$	133	0.5	$\text{C}_4\text{FH}_7\text{N}_2\text{P}$
169	2.1	$\text{C}_2\text{F}_6\text{P}$	132	18.7	$\text{C}_2\text{F}_3\text{H}_6\text{NP}$
160	1.6	$\text{C}_3\text{F}_4\text{H}_3\text{NP}$	121	1.4	$\text{C}_3\text{FH}_7\text{N}_2\text{P}$
157	1.8	$\text{C}_4\text{F}_2\text{H}_{12}\text{N}_2\text{P}$	119	5.1	CF_4P
144	2.0	$\text{C}_3\text{F}_3\text{H}_6\text{NP}$	117	5.1	$\text{CF}_3\text{H}_3\text{NP}$
132	5.5	$\text{C}_2\text{F}_3\text{H}_6\text{NP}$	116	0.6	$\text{CF}_3\text{H}_2\text{NP}$
126	1.0	$\text{C}_4\text{F}_2\text{H}_{12}\text{N}_2$	112	1.8	$\text{C}_2\text{F}_2\text{H}_5\text{NP}$

(continued.....)

TABLE VII (continued)

$(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$			$(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$		
110	1.0	$\text{C}_2\text{F}_2\text{H}_3\text{NP}$	105	1.4	$\text{C}_3\text{FH}_5\text{NP}$
94	6.5	$\text{C}_2\text{FH}_6\text{NP}$	103	9.6	$\text{CF}_3\text{H}_3\text{P}$
69	6.4	CF_3	101	14.4	CF_3HP
58	2.1	$\text{C}_2\text{H}_6\text{N}_2$	94	7.6	$\text{C}_2\text{FH}_6\text{NP}$
51	1.2	FHP	86	1.5	$\text{CF}_2\text{H}_5\text{P}$
44	3.0	$\text{C}_2\text{H}_6\text{N}$	85	3.8	$\text{CF}_2\text{H}_4\text{P}$
43	1.6	$\text{C}_2\text{H}_5\text{N}$	84	4.0	$\text{CF}_2\text{H}_3\text{P}$
42	6.5	$\text{C}_2\text{H}_4\text{N}$	83	1.8	$\text{CF}_2\text{H}_2\text{P}$
32	5.2	HP	82	4.1	CF_2HP
31	0.7	CF	69	3.3	CF_3
			66	4.5	CFH_4P
			49	3.7	H_4NP
			47	5.1	H_2NP
			44	3.5	$\text{C}_2\text{H}_6\text{N}$
			43	2.6	$\text{C}_2\text{H}_5\text{N}$
			42	12.0	$\text{C}_2\text{H}_4\text{N}$
			35	3.6	FH_2N
			31	3.2	CF

(footnotes to table continued
on next page)

(footnotes to table continued
on next page)

(a) Intensities are expressed relative to the total ionization defined as $\sum_n$ (intensity) for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak.

(b) The identity of these peaks were established by mass measurement under high resolution

<u>Ion</u>	<u>m/e calcd</u>	<u>m/e obsd</u>
$C_6F_6H_{12}N_2P^+$	257.0640	257.0644
$C_4F_7H_6NP^+$	232.0125	232.0118

(c) The identity of these peaks were established by mass measurement under high resolution

<u>Ion</u>	<u>m/e calcd</u>	<u>m/e obsd</u>
$C_5F_5H_{12}N_2P^+$	226.0656	226.0656
$C_5F_4H_{12}N_2P^+$	207.0672	207.0666
$C_3F_5H_6NP^+$	182.0157	182.0154

(d) Acid Hydrolysis

Hydrolysis of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ (0.084 g, 0.31 mmoles) with 0.5 cc of degassed distilled H_2O initially adjusted to a $\text{pH} \approx 1$ at room temperature for 24 hours gave CF_3H (0.006 g, 0.09 mmoles). The ^{19}F nmr spectrum of the remaining aqueous solution indicated the presence of $(\text{CF}_3)_2\text{PO}_2^-$ and $\text{CF}_3\text{PO}_3\text{H}^-$ ions in the ratio of 2:1.³⁸

(e) Reaction of the Monofluorophosphorane with Hydrogen Chloride.

A sample of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ (0.202 g, 0.73 mmoles) was allowed to react with an excess of anhydrous HCl (0.587 g, 21.9 mmoles) for 10 minutes at room temperature. Vacuum fractionation of the volatile products gave a mixture (0.019 g) trapping at -116°C which contained $(\text{CF}_3)_2\text{PCl}_3$ ²¹ and $(\text{CF}_3)_2\text{FPCl}_2$ ³² in the ratio 1 : 5 (by nmr spectroscopy) and a mixture (0.528 g) of mainly HCl with at least two additional unidentified compounds which also trapped at -196°C .

2. Preparation and Characterization of Trifluoromethyl-bis(dimethylamino)difluorophosphorane(a) Preparation from $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$

A sample of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.099 g, 0.30 mmoles)

was heated for 2 hours at 215°C. Vacuum fractionation gave in the -96°C trap a mixture (0.036 g) which was shown by nmr spectroscopy to contain the new phosphorane $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.033 g, 0.15 mmole) in a 50% yield and $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ ³⁶ (0.003 g, 0.01 mmole). Pure $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ was obtained by careful refractionation of the initial -96°C fraction. Analysis of the mixture (0.031 g) trapping at -196°C showed the presence of CF_3H , $(\text{CF}_2)_3$ ⁴⁶ and $(\text{CF}_2)_2$ ⁴⁷ in the molar ratio 1 : 2.4 : 2.7 (by nmr spectroscopy). The brown solid which remained in the reaction vessel did not dissolve in CD_3CN and was not identified.

(b) Physical Properties of $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$

The compound melts at -17°C forming a colourless liquid which is stable over long periods of time at room temperature. $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ was characterized by its spectroscopic properties (ir Table VI, nmr Table XIII) by mass spectroscopy (Table VII) and also by the chemical reaction described below.

(c) Alkaline Hydrolysis of the Difluorophosphorane

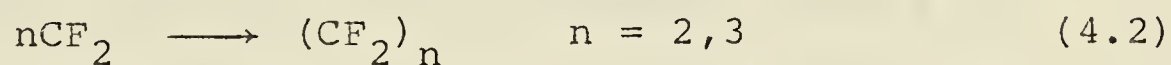
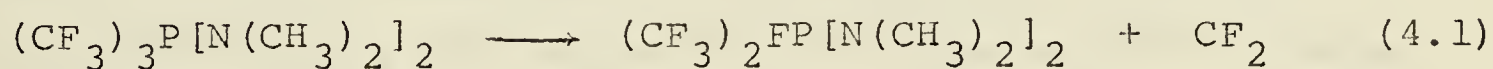
Hydrolysis of $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ (0.025 g, 0.11 mmole) with 0.3 mls of degassed 10% NaOH solution was carried out in an nmr tube at room temperature for 48 hours. Nmr spectra of the aqueous solution indicated the presence of $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$ (vide infra) and the CF_3PO_3^-

ion ³⁸ in the ratio 1 : 1.5 and an as yet unidentified species giving rise to a singlet in the ¹⁹F nmr at $\phi_F = 121.3$ ppm. Fractionation of the volatile contents of the nmr tube gave no CF₃H.

3. Results and Discussion

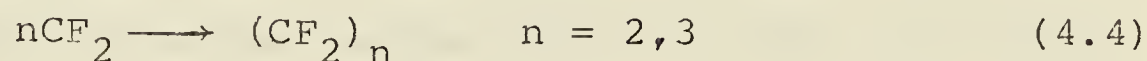
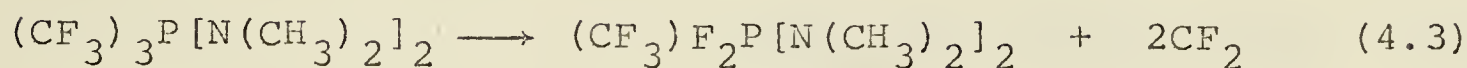
The thermal decomposition of trifluoromethylphosphoranes leading to the formation of difluorocarbene has been observed for (CF₃)₃PF₂, (CF₃)₂PF₃ and CF₃PF₄. In the absence of a trapping agent the CF₂ radical forms both the dimer C₂F₄ and the trimer C₃F₆ in varying proportions depending on the pyrolysis conditions.²⁶

The pyrolysis of (CF₃)₃P[N(CH₃)₂]₂ proceeded similarly. After 2½ hours at 100°C, the compounds (CF₃)₂FP[N(CH₃)₂]₂, (CF₂)₃⁴⁶ and (CF₂)₂⁴⁷ were produced according to the eqn (4.1, 4.2).



Total yields of the difluorocarbene polymers corresponded well with the yield of (CF₃)₂FP[N(CH₃)₂]₂ (75%) although the relative amounts of the dimer and trimer varied somewhat between different preparations. Also found in the products were small amounts of (CF₃)₂PN(CH₃)₂³⁶, (CF₃)₃P²⁰ and CF₃H which arise from secondary, unknown decomposition pathways.

At 215° for 2 hours pyrolysis of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ gave $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$, $(\text{CF}_2)_3$ and $(\text{CF}_2)_2$ according to the eqn (4.3, 4.4).



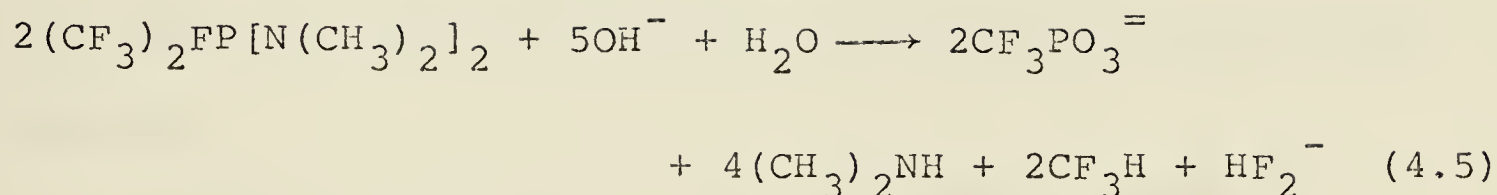
As in the previous case, $(\text{CF}_3)_2\text{PN}(\text{CH}_3)_2$ and CF_3H were again present in very small amounts.

Attempts to prepare $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ by heating $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ for 10 days at 100°C resulted in the recovery of unchanged starting materials. Heating of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ for 2 days at 200°C gave large amounts of black involatile solid which did not dissolve in CD_3CN and a small amount of unidentified volatile material.

In an attempt to prepare the third member in this series of CF_2 eliminations, $\text{F}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$, a sample of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ was heated for 48 hours at 200°C. Large amounts of black involatile solid and small amounts of CF_3H and other unidentified volatiles resulted and were not investigated. The compound $\text{F}_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ has been reported⁴⁸ previously but no mention was made of its stability under the conditions of this experiment.

The alkaline hydrolysis of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ gave one molar equivalent of CF_3H , two molar equivalents of $(\text{CH}_3)_2\text{NH}$ and one molar equivalent of CF_3PO_3^- according

to eqn (4.5) .



The hydrolysis in acidic medium ($\text{pH} \approx 1$) gave 0.29 molar equivalents of CF_3H , 0.33 molar equivalents of $\text{CF}_3\text{PO}_3\text{H}^-$ and 0.67 molar equivalents of $(\text{CF}_3)_2\text{PO}_2^-$. The formation of CF_3H and $\text{CF}_3\text{PO}_3\text{H}^-$ ion under these conditions may again be explained by the localized base reaction of the leaving $(\text{CH}_3)_2\text{NH}$ and F^- groups as was proposed for the $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ hydrolysis.

The alkaline hydrolysis of $(\text{CF}_3)_2\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ gave no CF_3H and a mixture of CF_3PO_3^- and $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$ were found in the solution. The presence of $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$ indicates the resistance of the P-N linkage to hydrolysis in this compound. A similar result was observed upon attempted hydrolysis of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+$ which gave only $\text{OP}[\text{N}(\text{CH}_3)_2]_3$ as discussed in more detail in Chapter 5.

The reaction of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ with excess HCl proceeded in very low yield to form $(\text{CF}_3)_2\text{FPCl}_2$. This compound was identified by comparison of its ir spectrum with that reported in the literature.³² The ^{19}F nmr spectrum at room temperature showed a doublet of doublets ($\phi_{\text{F}} = 77.0$ ppm, $^2J_{\text{FP}} = 184$ Hz, $^3J_{\text{FF}} = 14$ Hz), but the compound was present in a too small a quantity to allow

observation of the fluorine atom signal which would be split into a doublet of septets. Also produced in this reaction were small amounts of $(\text{CF}_3)_2\text{PCl}_3$ and several unidentified species.

The ir spectrum of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ gave the expected CF_3 and CH_3 absorptions and also gave peaks at 1085 and 1004 cm^{-1} , 755 cm^{-1} , 678 and 662 cm^{-1} which were attributed to asymmetric C_2N stretching, P-F stretching and asymmetric N_2P stretching vibrations. The ions at $m/e = 232$ and $m/e = 257$ in the mass spectrum were found by accurate mass measurement to be the $\text{C}_4\text{F}_7\text{H}_6\text{NP}^+$ and $\text{C}_6\text{F}_6\text{H}_{12}\text{N}_2\text{P}^+$ ions whose formation can be explained by the loss of $\text{N}(\text{CH}_3)_2$ and F respectively from the unobserved parent $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$.

The room temperature ^1H nmr spectrum (Figure 5) of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ shows a doublet of doublets of septets arising from the coupling of the protons to a phosphorus atom ($^3J_{\text{PH}} = 11.6 \text{ Hz}$), to a fluorine atom ($^4J_{\text{FH}} = 3.1 \text{ Hz}$) and to six equivalent fluorine atoms ($^5J_{\text{FH}} = 0.6 \text{ Hz}$) thus confirming the presence of two CF_3 groups and one F atom on phosphorus. The ^1H nmr spectrum remained unchanged on cooling the sample to -70°C thus indicating the $\text{N}(\text{CH}_3)_2$ groups were magnetically equivalent to this temperature, probably as a result of a rapid pseudorotatory averaging process.

The room temperature ^{19}F nmr spectrum of

FIGURE 5

The ^1H spectrum and part of the ^{19}F nmr spectrum of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$. The ^1H nmr spectrum was measured at 100 MHz on a CCl_3F solution of the compound at 40°C . The frequency scale is measured relative to TMS with positive sign denoting lower field. The ^{19}F nmr spectrum of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ was measured at 56.4 MHz on a C_6F_6 solution at 75°C . Only the CF_3 portion of the spectrum is illustrated. The frequency scale is measured relative to CFCl_3 with positive sign denoting resonances to higher field of the standard. Calculated spectra using the parameters given in Table XIII are shown as stick diagrams for each spectrum.

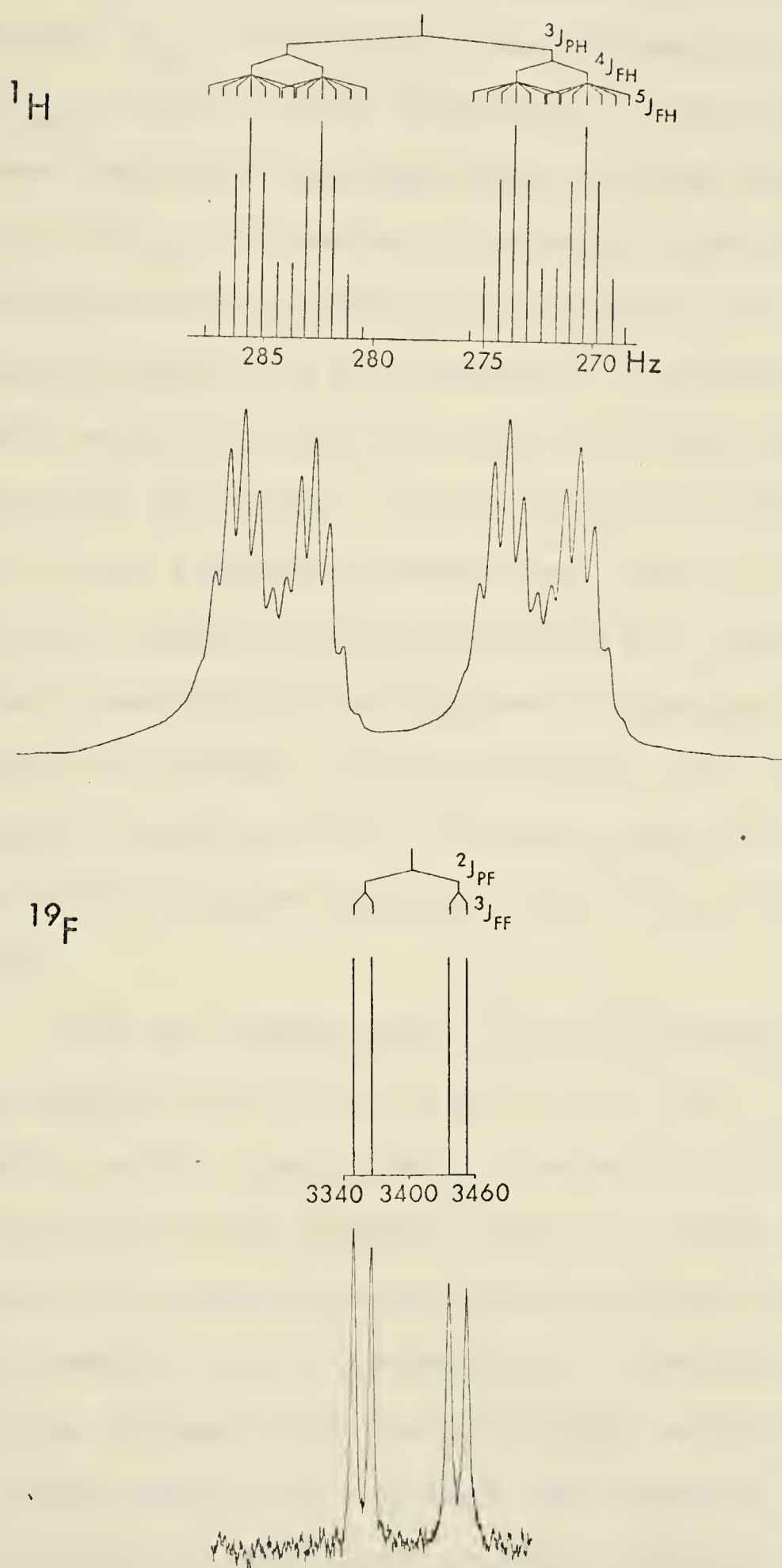


FIGURE 5. The ^1H and ^{19}F nmr Spectra of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$

$(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ (Figure 6) shows a broad doublet with a coupling $^2J_{\text{FP}} = 88$ Hz and a second doublet with a coupling of $^1J_{\text{FP}} = 790$ Hz which integrated in the ratio of 6 : 1. It was therefore concluded that at room temperature an average $^2J_{\text{PF}}$ is observed, presumably also as a result of a pseudorotatory process since the more electronegative fluorine atom would be expected¹¹ to occupy an axial environment requiring the CF_3 groups to occupy both axial and equatorial positions. Heating to 75°C should increase the rate of the averaging process and lead to a sharpening of the broad doublet arising from the CF_3 substituents. Sufficient resolution was obtained to observe, at 75°C , a doublet of doublets (Figure 5) which are assigned to the averaged coupling of CF_3 fluorine atoms to the phosphorus atom and the unique fluorine atom ($^2J_{\text{PF}} = 86$ Hz $^3J_{\text{FF}} = 16$ Hz).

The low temperature ^{19}F nmr spectrum gave rise to four chemically shifted regions at -90°C . Three of these signals, which integrated in the ratio of 1 : 2 : 3, can be assigned to CF_3 groups (Figure 6) which suggests that the two CF_3 groups are divided into axial and equatorial environments at this temperature. Further, the splitting patterns suggest that the rotational motion of one of the CF_3 groups about the P-C bond axis appears to have been slowed down or restricted in such a manner as to make its fluorine atoms non-equivalent. Thus the area of intensity

FIGURE 6

The temperature dependent ^{19}F nmr spectra of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$. The 75°C spectrum was measured at 56.4 MHz on a C_6F_6 solution while the 40° , 10° , -30° and -90°C spectra were measured at 94.1 MHz on a CF_2Cl_2 solution. The frequency scale is measured relative to CFCl_3 with positive sign denoting resonances to high field of the standard.

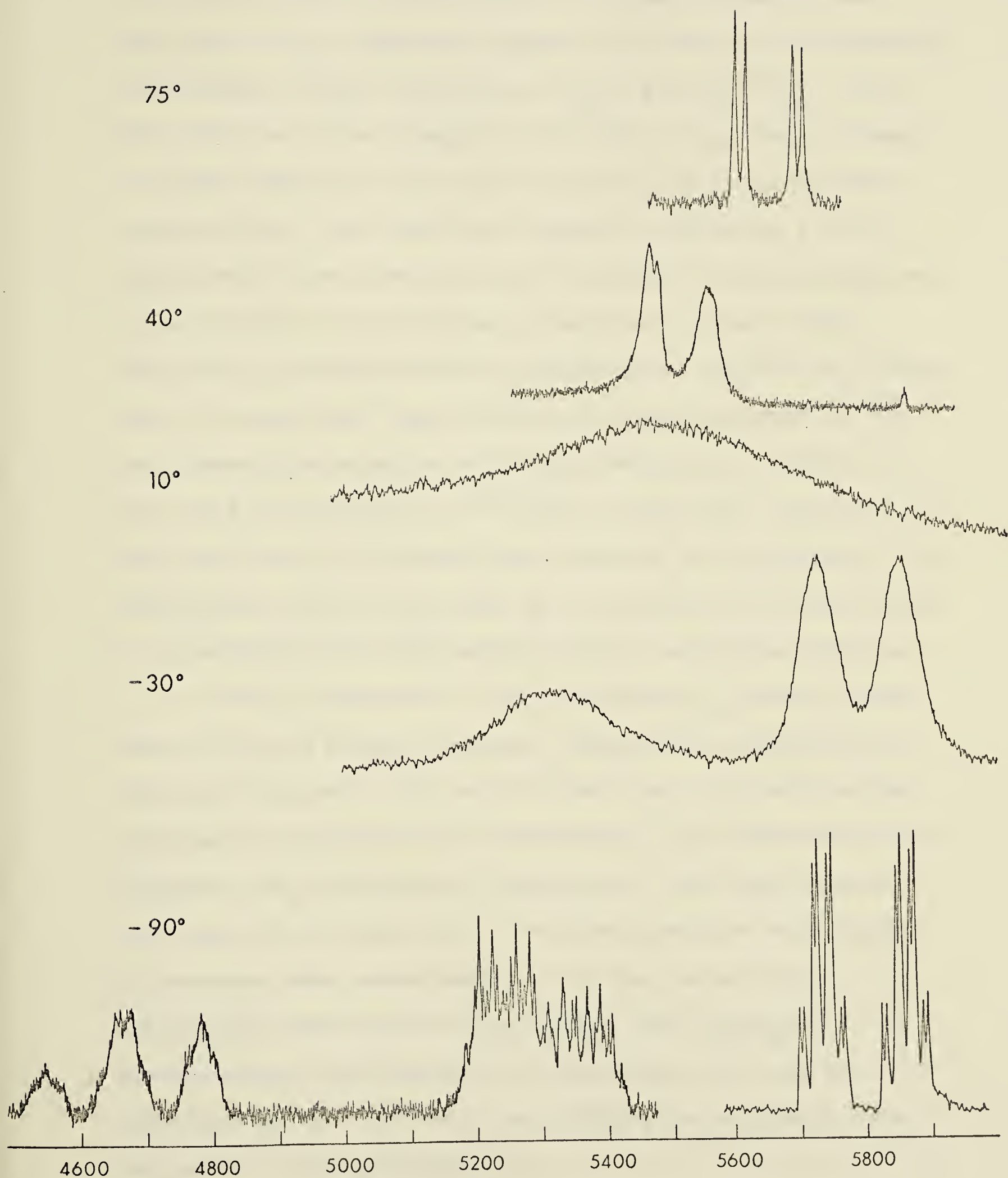


FIGURE 6. Temperature Dependence of the ^{19}F nmr Spectra of $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$

3 is due to the CF_3 group which is freely rotating and this area of the spectrum appears as a doublet of doublets of quartets ($^2J_{\text{FP}} = 125.5 \text{ Hz}$, $^3J_{\text{FF}} = 6.0 \text{ Hz}$, $^4J_{\text{FF}} = 21.5 \text{ Hz}$) with the latter coupling constant, $^4J_{\text{FF}}$, being caused by equal coupling to the two fluorine environments described below. The other two signals (intensity 1 : 2) showed much more complex fine structure, and both appeared to be coupled to each other as well as to the P atom, the fluorine atom attached to phosphorus and the CF_3 group. These features are very similar to those observed in the low temperature spectra of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ (Chapter 3) and $(\text{CF}_3)_3\text{P}[\text{OSi}(\text{CH}_3)_3]_2$ ³³ which, it has been suggested,³³ are also due to the restricted rotation of CF_3 groups. No conclusions can yet be drawn as to whether it is the axial or equatorial CF_3 group which suffers restricted rotation.

The ir spectrum of $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ shows bands due to CF_3 and $\text{N}(\text{CH}_3)_2$ groups. Absorptions appearing at 1170 and 1023 cm^{-1} , 810 and 771 cm^{-1} and 673 cm^{-1} can be assigned to asymmetric C_2N stretching, P-F stretching and asymmetric N_2P stretching vibrations. The ions at m/e 226, m/e 207 and m/e 182 in the mass spectrum were found by accurate mass measurement to be the parent ion $\text{C}_5\text{F}_5\text{H}_{12}\text{N}_2\text{P}^+$ and the ions $\text{C}_5\text{F}_4\text{H}_{12}\text{N}_2\text{P}^+$ and $\text{C}_3\text{F}_5\text{H}_6\text{NP}^+$ respectively; the formation of the latter two can be explained by the loss of F and $\text{N}(\text{CH}_3)_2$ respectively from the parent $(\text{CF}_3)\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$.

The room temperature ^1H nmr spectrum of $(\text{CF}_3)_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ shows a doublet of triplets arising from methyl group protons coupling to phosphorus ($^3J_{\text{PH}} = 10.4$ Hz) and to the two fluorine atoms ($^4J_{\text{FH}} = 2.7$ Hz) bonded to phosphorus. The absence of any fine structure in the expansion of this doublet of triplets indicates that the magnitude of coupling between the fluorine atoms on the CF_3 group and the protons in the $\text{N}(\text{CH}_3)_2$ substituents is below the resolution of the instrument. Typical values for this coupling $^5J_{\text{FH}}$ obtained from other related compounds in this study range from 0.60 Hz to 1.09 Hz.

The room temperature ^{19}F nmr spectrum of $(\text{CF}_3)_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ appears as a doublet of triplets and a doublet of broad multiplets in the intensity ratio of 3 : 2 respectively. The signal of intensity 3 arises from the CF_3 group which couples to phosphorus $^2J_{\text{PF}} = 150$ Hz and to the fluorine atoms $^3J_{\text{FF}} = 17.8$ Hz while the signal of intensity 2 arises from the two directly bound fluorine atoms coupled to phosphorus $^1J_{\text{PF}} = 794$ Hz, to the CF_3 group and to the two $\text{N}(\text{CH}_3)_2$ groups. The latter two couplings should split each component of the doublet into a quartet of thirteen line multiplets, but the low intensity and width of these signals did not permit sufficient resolution to confirm this. The doublet of triplets arising from the CF_3 group showed some asymmetry in peak height and intensity, a feature which was particularly evident in the

triplet nearest the fluorine atom signal. Although attempts to compute a spectrum showing the same intensity features as that observed were unsuccessful, it seems likely that the asymmetry results from a second order spectrum of the A_2B_3X type.

CHAPTER V

REACTIONS OF BIS (TRIFLUOROMETHYL) TRICHLOROPHOSPHORANE $(\text{CF}_3)_2\text{PCl}_3$ AND TRIFLUOROMETHYLTETRACHLOROPHOSPHORANE CF_3PCl_4 WITH DIMETHYLAMINE

The successful isolation of dimethylaminophosphoranes arising from the reaction of $(\text{CH}_3)_2\text{NH}$ with $(\text{CF}_3)_3\text{PCl}_2$ ²⁰ suggested that an investigation of the reactions of $(\text{CF}_3)_2\text{PCl}_3$ ²¹ and CF_3PCl_4 ²³ with varying amounts of dimethylamine might result in further insight into the formation of these phosphoranes and possibly some additional phosphoranes. A new phosphorane bis(trifluoromethyl)dimethylaminodichlorophosphorane $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ and a phosphonium salt trifluoromethyltris(dimethylamino)phosphonium chloride $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$ which resulted from these studies are described herein.

1. Preparation and Characterization of Bis(trifluoromethyl)-
dimethylaminodichlorophosphorane, $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$

(a) Preparation

Using the apparatus described in Figure 1 gaseous $(\text{CH}_3)_2\text{NH}$ (0.132 g, 2.93 mmoles) was allowed to react with $(\text{CF}_3)_2\text{PCl}_3$ (0.274 g, 0.99 mmoles) at room temperature for 30 minutes. Vacuum fractionation of the volatile products afforded a mixture (0.139 g) which trapped at -45°C and was shown by nmr spectroscopy to contain $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ (0.133 g, 0.47 mmoles) and $(\text{CF}_3)_2\text{PCl}_3$ (0.006 g, 0.02 mmoles).

Also obtained was $(\text{CF}_3)_2\text{PCl}_3$ (0.059 g, 0.21 mmoles) which was trapped at -96°C , $(\text{CH}_3)_2\text{NH}$ (0.036 g, 0.80 mmoles) which was trapped at -116°C and CF_3H (0.009 g, 0.13 mmoles) which was trapped at -196°C . Pure $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ was obtained by further careful refractionation of the crude -45°C mixture.

(b) Physical Properties

The compound $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ is a relatively involatile white solid at room temperature which was stable for a number of weeks at room temperature. The compound was characterized by the chemical reactions described below and its spectroscopic properties (ir, Table VIII, nmr, Table XIII and mass spectroscopy Table IX). The identity of the ion at m/e 248 was established by accurate mass measurements [obsd m/e 247.9833 calcd m/e 247.9830] to be the $\text{C}_4\text{F}_6^{35}\text{ClH}_6\text{NP}^+$ ion.

(c) Reaction with Water

Hydrolysis of $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ (0.105 g, 0.37 mmoles) with approximately 0.8 mls of degassed distilled water at room temperature for 48 hrs gave CF_3H (0.001 g, 0.014 mmoles). The nmr spectrum of the remaining aqueous solution indicated the presence of the $(\text{CF}_3)_2\text{PO}_2^-$ ion.³⁸

(d) Alkaline Hydrolysis

$(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ (0.160 g, 0.56 mmoles) was combined with 0.8 mls of 10% NaOH solution and allowed to

TABLE VIII

Infrared Spectrum of $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ ^{a,b}

		<u>Assignment</u>
3031 (vw)	}	$\nu(\text{C-H})$
2954 (w)		
2945 (w, sh)		
2875 (w)		
2832 (w)		
1467 (w)	}	$\delta(\text{CH}_3) + \nu(\text{C-N})$
1328 (w)		
1291 (w)		
1204 (m)	}	$\nu(\text{C-F})$
1185 (s)		
1168 (s)		
1162 (s, sh)		
1153 (s, sh)		
1148 (s)		
1144 (s)		
990 (m)		$\nu_{\text{as}}(\text{C}_2\text{N})$
708 (m)		$\delta_{\text{s}}(\text{CF}_3)$
590 (m)	}	$\nu_{\text{as}}(\text{N}_2\text{-P})$
558 (w)		$\nu(\text{P-Cl})$
536 (m)		$\delta_{\text{as}}(\text{CF}_3)$

(a) All values in cm^{-1}

(b) Abbreviations: ν = stretching, δ = deformation, s = strong, m = medium, w = weak, v = very, sh = shoulder, as = antisymmetric, s = symmetric.

TABLE IX

Mass Spectrum of $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$

<u>m/e</u>	<u>Rel. int.^a</u>	<u>Assignment</u>	<u>m/e</u>	<u>Rel. int.^a</u>	<u>Assignment</u>
250	.01	$\text{C}_4\text{F}_6\text{ClH}_6\text{NP}$	101	0.6	CF_3HP
248 ^b	.03		99	0.7	$\text{CF}_2\text{H}_4\text{NP}$
243	.011	$\text{C}_2\text{F}_6\text{Cl}_2\text{P}$	94	9.1	$\text{C}_2\text{FH}_6\text{NP}$
241	.069		91	0.6	$\text{C}_2\text{FH}_3\text{NP}$
239	.100		90	1.4	$\text{C}_2\text{FH}_2\text{NP}$
229	4.0	$\text{C}_4\text{F}_7\text{H}_3\text{NP}$	85	3.8	$\text{CF}_2\text{H}_4\text{P}$
228	0.3	$\text{C}_4\text{F}_7\text{H}_2\text{NP}$	81	0.4	C_2F_3
206	0.02	$\text{C}_2\text{F}_6\text{ClP}$	76	0.6	CFNP
204	0.06		69	11.6	CF_3
182	0.5	$\text{C}_3\text{F}_5\text{H}_6\text{NP}$	60	0.6	CH_3NP
178	0.5	$\text{C}_3\text{F}_5\text{H}_2\text{NP}$	57	0.6	CNP
160	6.9	$\text{C}_3\text{F}_4\text{H}_3\text{NP}$	50	0.7	CF_2
151	0.6	$\text{C}_2\text{F}_5\text{HP}$	47	4.9	H_2NP
135	0.4	$\text{CF}_4\text{H}_2\text{NP}$	44	2.0	$\text{C}_2\text{H}_6\text{N}$
132	0.6	$\text{C}_2\text{F}_3\text{H}_6\text{NP}$	43	2.4	$\text{C}_2\text{H}_5\text{N}$
128	0.8	$\text{C}_2\text{F}_3\text{H}_2\text{NP}$	42	8.4	$\text{C}_2\text{H}_4\text{N}$
119	0.7	CF_4P	41	0.8	$\text{C}_2\text{H}_3\text{N}$
110	9.9	$\text{C}_2\text{F}_2\text{H}_3\text{NP}$	40	1.2	$\text{C}_2\text{H}_2\text{N}$
			38	0.9	F_2
			36	3.3	FH_3N
			32	18.9	CFH
			31	1.0	CF

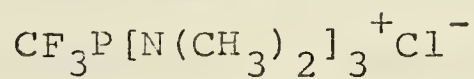
Footnotes to Table IX

- (a) Intensities are expressed relative to the total ionization defined as $\sum_n(\text{intensity})$ for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak.
- (b) The identity of this peak was established by mass measurement under high resolution.

<u>Ion</u>	<u>m/e calc.</u>	<u>m/e obs.</u>
$\text{C}_4\text{F}_6^{35}\text{ClH}_6\text{NP}$	247.9830	247.9833

react for 48 hrs at room temperature. Fractional condensation of the volatile products in vacuum gave CF_3H (0.040 g, 0.57 mmoles). Nmr spectra of the remaining aqueous solution indicated the presence of the CF_3PO_3^- ion.³⁸

2. Preparation and Characterization of Trifluoromethyl-tris(dimethylamino)phosphonium chloride



(a) Preparation from $(\text{CF}_3)_2\text{PCl}_3$ and $(\text{CH}_3)_2\text{NH}$

A sample of $(\text{CF}_3)_2\text{PCl}_3$ (1.077 g, 3.91 mmoles) was allowed to react with $(\text{CH}_3)_2\text{NH}$ (1.081 g, 24.02 mmoles) for 4 days at room temperature. Vacuum fractionation of the volatile products gave $(\text{CH}_3)_2\text{NH}$ (0.185 g, 4.11 mmoles) which was collected at -116°C and CF_3H (0.283 g, 4.04 mmoles) which was collected at -196°C . The white involatile solid which remained in the reaction tube was identified as a mixture of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$ and $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$ salts as described below.

(b) Preparation from CF_3PCl_4 and $(\text{CH}_3)_2\text{NH}$

The compound CF_3PCl_4 (0.239 g, 0.99 mmoles) and $(\text{CH}_3)_2\text{NH}$ (0.452 g, 10.04 mmoles) were allowed to react at room temperature for 24 hours. Fractionation of the volatile products gave $(\text{CH}_3)_2\text{NH}$ (0.182 g, 4.06 mmoles) which was collected at -116°C and a minute trace of CF_3H which was collected at -196°C . The white involatile solid which remained in the reaction tube was similarly identi-

fied as a mixture of the $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$ and $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$ salts.

(c) Characterization of the Phosponium Salt

Inspection of the ir (Table X), nmr (Table XIII) and mass spectrum (Table XI) of the white involatile solid product in (a) and (b) above, together with the determined stoichiometries of these reactions suggested that the white solid was a mixture of dimethylammonium chloride and a compound described by the formula " $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3$ ". Attempted separation of these species by their solubility properties in CCl_4 , ether, CHCl_3 and n-pentane were all unsuccessful. Addition of an aqueous KPF_6 solution to an aqueous solution of the above mixture resulted in the formation of a white precipitate identified as $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{PF}_6^-$. The salt analyzed for C = 22.31, H = 4.97, F = 45.46, N = 10.95, P = 15.67%, calcd for $\text{C}_7\text{H}_{18}\text{F}_9\text{N}_3\text{P}_2$, C = 22.29, H = 4.82, F = 45.33, N = 11.12, P = 16.42%. Of the several solvents tested, only CD_3CN dissolved this fluorophosphate salt and the nmr spectra of the resultant solution showed the following nmr signals which were given the indicated assignments. The ^{19}F nmr showed a doublet of multiplets [$\phi_{\text{F}} = 60.8$ ppm, $^2J_{\text{PF}} = 108$ Hz] due to a CF_3P group and a doublet [$\phi_{\text{F}} = 73.0$ ppm, $^1J_{\text{PF}} = 707$ Hz] due to the PF_6^- ion. These signals integrated in the ratio of 1:2 respectively. The ^1H nmr spectrum showed a doublet of quartets [$\tau_{\text{H}} = 7.24$,

TABLE X

Infrared Spectra of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{PF}_6^-$ and $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$

$\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{PF}_6^{-\text{a,b}}$	$\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$ $+ (\text{CH}_3)_2\text{NH}_2^+\text{Cl}^{-\text{a,b}}$		
3010 (vw)		$\left\{ \begin{array}{l} \nu(\text{C-H}) \\ \nu(\text{C-H}) \end{array} \right.$	$(\text{CH}_3)_2\text{NH}_2^+$
2935 (w)	3000 (s,br)		$(\text{CH}_3)_2\text{N}^+$
2877 (w,sh)	2700 (s,br)		
2840 (w)	2420 (vs)		
1640 (w)	1635 (w)		PF_6^-
	1585 (w)		$(\text{CH}_3)_2\text{NH}_2^+$
1493 (m)	1490 (w)	$\left\{ \begin{array}{l} \delta(\text{CH}_3) \\ \nu_s(\text{C}_2\text{N}) \end{array} \right.$	
1470 (m)	1469 (m)		
1459 (m)	1455 (w)		
1319 (s)	1316 (vw)		
	1255 (vw)		$(\text{CH}_3)_2\text{NH}_2^+$
1199 (s)	1199 (s)	$\left\{ \begin{array}{l} \nu(\text{C-F}) \end{array} \right.$	
1174 (s)	1172 (s)		
1155 (s,sh)			
1147 (vs)	1146 (vs)		
1070 (s)	1066 (m)		$(\text{CH}_3)_2\text{NH}_2^+$
	1020 (s)		$\nu_{\text{as}}(\text{C}_2\text{N})$
1010 (vs)	1010 (vs)		$(\text{CH}_3)_2\text{NH}_2^+$
	883 (vs)		PF_6^-
874 (vs,sh)			$(\text{CH}_3)_2\text{NH}_2^+$
	864 (vs)		$\delta_s(\text{CF}_3)$
767 (m)	769 (w)		$\nu_{\text{as}}(\text{N}_2\text{P})$
652 (m)	653 (m)		PF_6^-
575 (s)			

(a) All values in cm^{-1} (b) Abbreviations: ν = stretching, δ = deformation, s = strong, m = medium, w = weak, v = very, sh = shoulder, as = antisymmetric, s = symmetric, br = broad.

TABLE XI

Mass Spectrum of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{PF}_6^-$

<u>m/e</u>	<u>Rel. Int.^a</u>	<u>Assignment</u>	<u>m/e</u>	<u>Rel. Int.^a</u>	<u>Assignment</u>
277	2.6	$\text{C}_5\text{F}_5\text{H}_{18}\text{N}_3\text{P}_2$	107	1.6	F_4P
233	1.3	$\text{C}_7\text{F}_3\text{H}_{18}\text{N}_3\text{P}$	105	4.3	$\text{C}_3\text{FH}_6\text{NP}$
232	15.4		94	5.6	$\text{C}_2\text{FH}_6\text{NP}$
231	1.3	$\text{C}_7\text{F}_3\text{H}_{17}\text{N}_3\text{P}$	82	1.6	CF_2HP
207	4.8	$\text{C}_5\text{F}_3\text{H}_{17}\text{N}_3\text{P}$	76	8.2	CFNP
188	2.0	$\text{C}_5\text{F}_3\text{H}_{12}\text{N}_2\text{P}$	60	4.6	CH_3NP
182	2.0	$\text{C}_6\text{FH}_{18}\text{N}_3\text{P}$	45	1.3	$\text{C}_2\text{H}_7\text{N}$
157	4.6	$\text{C}_4\text{F}_2\text{H}_{12}\text{N}_2\text{P}$	44	4.8	$\text{C}_2\text{H}_6\text{N}$
135	2.0	$\text{C}_5\text{H}_{16}\text{N}_2\text{P}$	42	3.6	$\text{C}_2\text{H}_4\text{N}$
119	26.8	$\text{C}_4\text{H}_{12}\text{N}_2\text{P}$	32	1.6	CFH

(a) Intensities are expressed relative to the total ionization defined as $\sum_n(\text{intensity})$ for all ions with mass greater than 30 whose intensity is greater than 2% of the base peak.

$^3J_{\text{PH}} = 10.5 \text{ Hz}$, $^5J_{\text{FH}} = 0.75 \text{ Hz}$] due to the $(\text{N}(\text{CH}_3)_2)$ group. All of these peaks except that due to the PF_6^- ion were present in the CD_3CN solution spectra obtained on the original salt mixture, which also possessed nmr signals typical of the $(\text{CH}_3)_2\text{NH}_2^+$ ion. The hydrogen to fluorine ratio in the cation was determined by nmr to be 6:1 using a measured quantity of fluorobenzene as an internal standard. The infrared spectrum appeared to be a composite of the spectra of KPF_6 and the original solid, with the $(\text{CH}_3)_2\text{NH}_2^+$ peaks removed. Alkaline hydrolysis of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{PF}_6^-$ (0.099 g, 0.26 mmoles) with 0.8 mls of degassed 10% NaOH solution at room temperature for $2\frac{1}{2}$ hours gave CF_3H (0.019 g, 0.27 mmoles). Proton and ^{19}F nmr spectrum of the remaining aqueous solution indicated the presence of the PF_6^- ion and $\text{OP}[\text{N}(\text{CH}_3)_2]_3$.

3. Reactions of $(\text{CF}_3)_2\text{PCl}_3$ and $(\text{CH}_3)_2\text{NH}$

Using the apparatus shown in Figure 1 several reactions were performed involving $(\text{CF}_3)_2\text{PCl}_3$ and varying molar ratios of $(\text{CH}_3)_2\text{NH}$ at room temperature. The reaction time was 30 minutes and throughout the series of reactions the amount of $(\text{CH}_3)_2\text{NH}$ was kept relatively constant to minimize the effect of its partial pressure on the reaction mechanism. Separation of the volatile products by vacuum fractionation gave, in the -45°C trap,

$(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ containing traces of $(\text{CF}_3)_2\text{PCl}_3$, in the -96°C trap, pure unreacted $(\text{CF}_3)_2\text{PCl}_3$, in the -116°C trap, pure unreacted $(\text{CH}_3)_2\text{NH}$ and in the -196°C trap, CF_3H . Details of the results of these experiments are summarized in Table XII and are presented graphically in Figure 7.

4. Reactions of CF_3PCl_4 and $(\text{CH}_3)_2\text{NH}$

Using the apparatus described in Figure 1, CF_3PCl_4 and $(\text{CH}_3)_2\text{NH}$ were allowed to react at room temperature for 24 hours in 1:2 and 1:6.5 ratios. The volatiles consisted of mainly unreacted CF_3PCl_4 (in the 1:2 reaction), or unreacted $(\text{CH}_3)_2\text{NH}$ (in the 1:6.5 reaction) plus small amounts of unidentified volatile products in both cases. The involatile solids from both reactions, when dissolved in CD_3CN , were shown by nmr spectroscopy to consist mainly of $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$, and $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$ with small amounts of several unidentified CF_3P containing compounds.

5. Results and Discussion

In a similar manner to the previously discussed dimethylamino-substitution reactions of $(\text{CF}_3)_3\text{PCl}_2$, the stepwise replacements of the Cl groups in $(\text{CF}_3)_2\text{PCl}_3$ could lead to the formation of $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ (I),

TABLE XII

Reaction Products of $(\text{CF}_3)_2\text{PCl}_3$ with $(\text{CH}_3)_2\text{NH}$

Ratio:	initial $(\text{CH}_3)_2\text{NH}$ (moles)	0.79	2.01	2.93	4.24	5.74	8.53	12.4
	initial $(\text{CF}_3)_2\text{PCl}_3$ (moles)							
Ratio:	reacted $(\text{CH}_3)_2\text{NH}$ (moles)	2.29	2.61	2.80	2.90	3.64	3.86	4.46
	reacted $(\text{CF}_3)_2\text{PCl}_3$ (moles)							
	% $(\text{CF}_3)_2\text{PCl}_3$ recovered	65.6	41.0	24.0	4.2	0	0	0
	% $(\text{CH}_3)_2\text{NH}$ recovered	0	23.2	27.3	35.0	36.5	54.9	64.1
	% $(\text{CF}_3)_2\text{PCl}_2\text{N}(\text{CH}_3)_2$	22.5	39.1	47.0	31.0	25.6	22.5	21.9
	% CF_3H	2.9	7.4	12.0	33.5	35.5	44.4	64.5

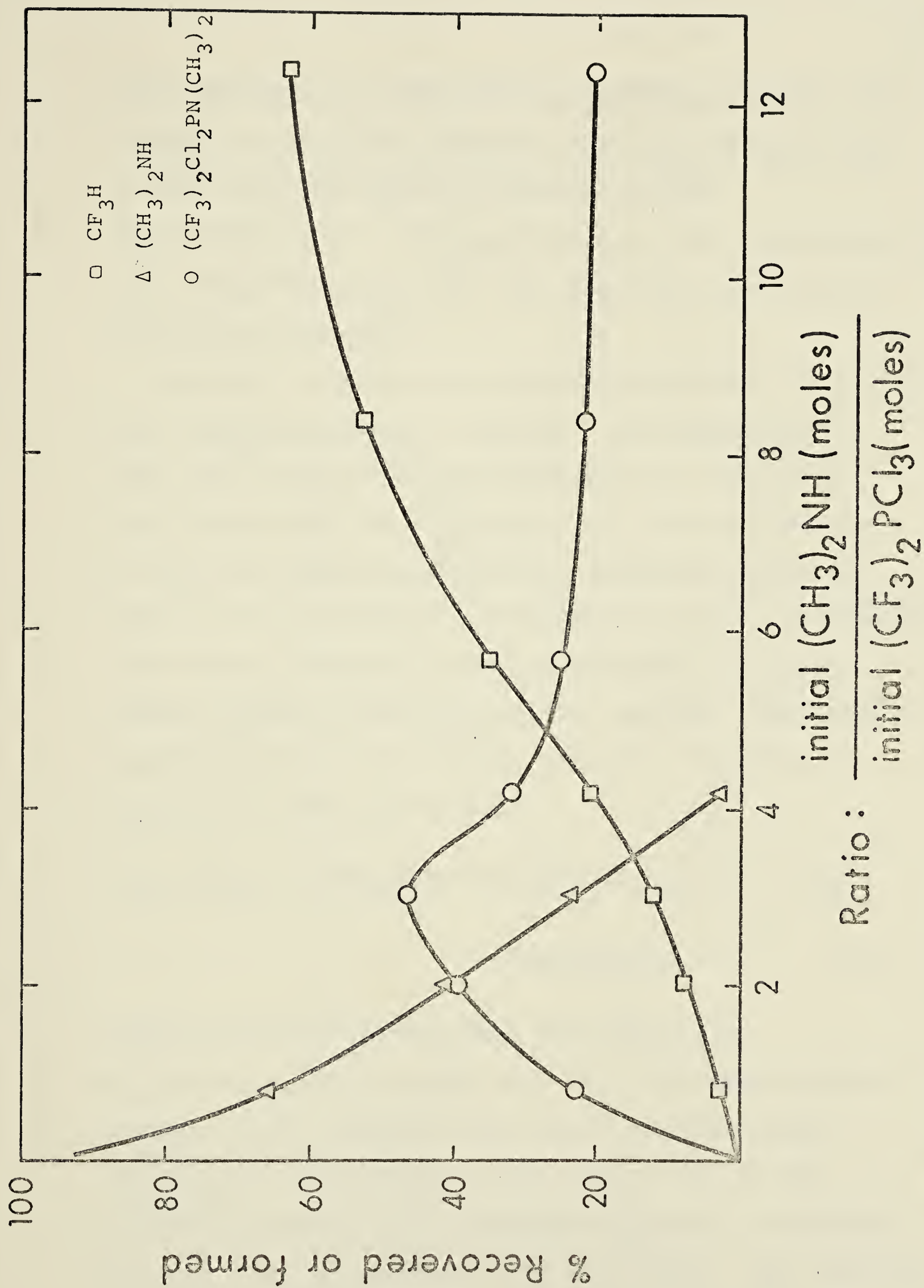
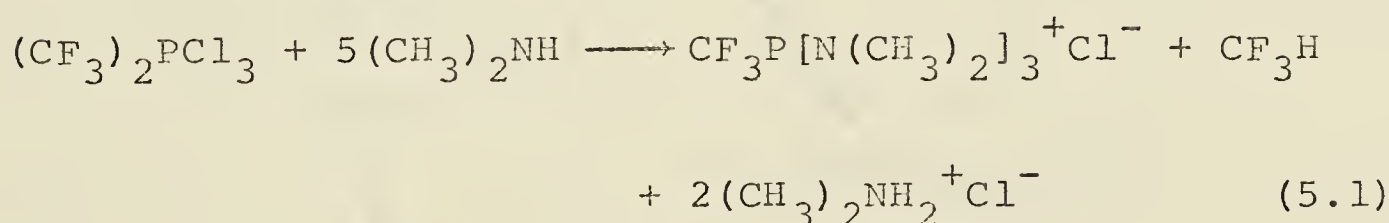


FIGURE 7. Graphic Representation of the Reaction of $(\text{CF}_3)_2\text{PCl}_3$ with $(\text{CH}_3)_2\text{NH}$

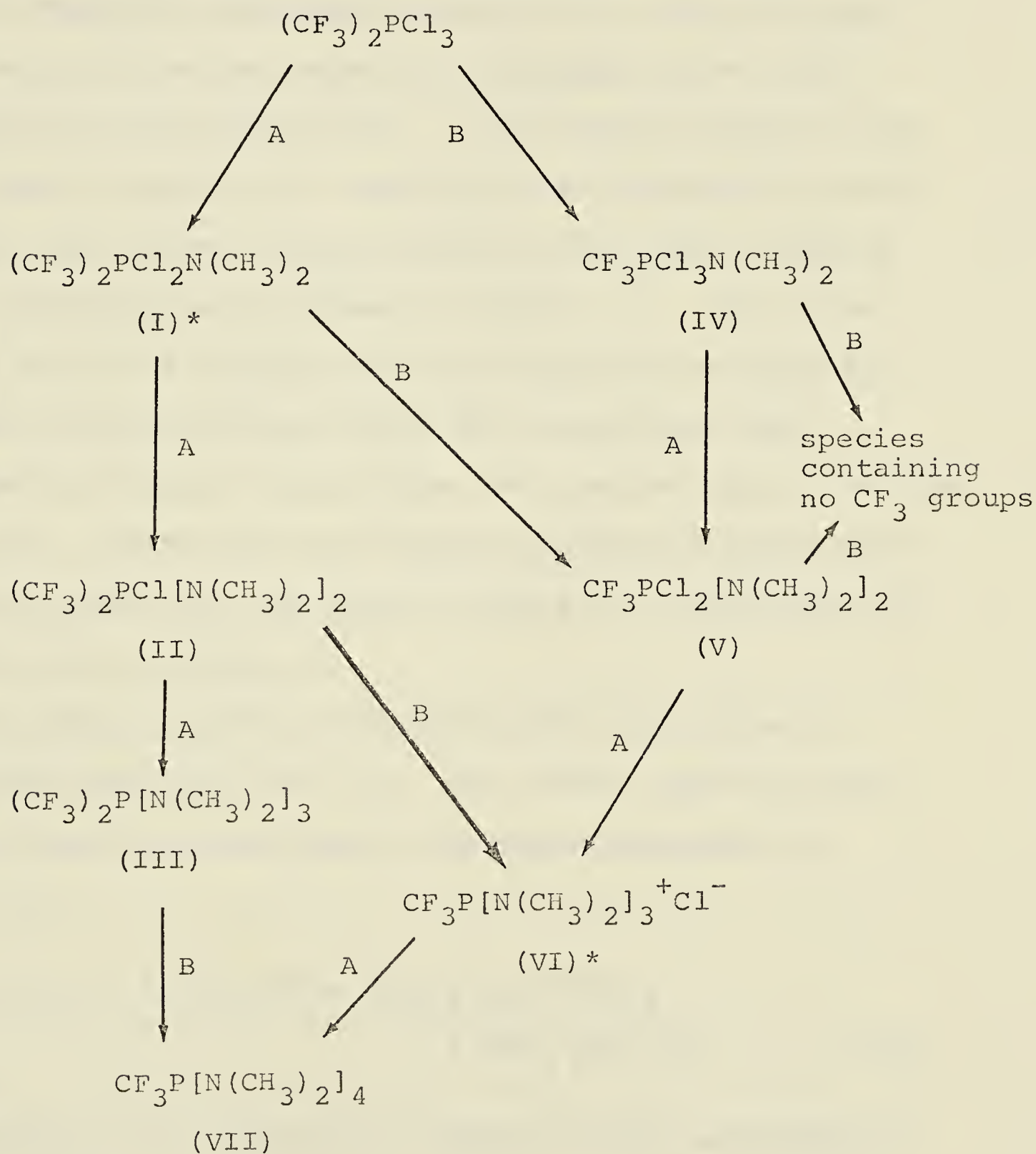
$(\text{CF}_3)_2\text{ClP}[\text{N}(\text{CH}_3)_2]_2$ (II) and $(\text{CF}_3)_2\text{P}[\text{N}(\text{CH}_3)_2]_3$ (III). Also possible would be the elimination of CF_3 groups as CF_3H as well as replacement of chlorine to give $\text{CF}_3\text{Cl}_3\text{PN}(\text{CH}_3)_2$ (IV), $\text{CF}_3\text{Cl}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ (V), $\text{CF}_3\text{ClP}[\text{N}(\text{CH}_3)_2]_3$ (VI), $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_4$ (VII) and compounds containing no CF_3 groups (Figure 8).

Several reactions were performed combining $(\text{CF}_3)_2\text{PCl}_3$ with various amounts of $(\text{CH}_3)_2\text{NH}$. The reaction of $(\text{CF}_3)_2\text{PCl}_3$ with six molar equivalents of $(\text{CH}_3)_2\text{NH}$ at room temperature for 4 days gave one molar equivalent of CF_3H , one molar equivalent of unreacted $(\text{CH}_3)_2\text{NH}$ and one molar equivalent of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$ (although this was not weighed it was the only CF_3P containing species found in the $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$ residue. The overall stoichiometry of the reaction described above can be expressed by the eqn (5.1).



Since no unreacted $(\text{CF}_3)_2\text{PCl}_3$ was found, and $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$ was the only CF_3P containing product formed, we can conclude that the CF_3H formed arose uniquely by elimination of only one of the two CF_3 groups on phosphorus and therefore compounds containing no CF_3 groups on phosphorus are not formed. The stability and ionic behavior of (VI) (vide infra) explains why

FIGURE 8

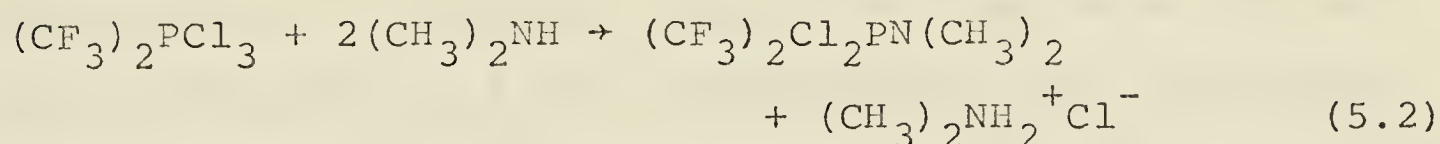
Possible Products from $(\text{CF}_3)_2\text{PCl}_3/(\text{CH}_3)_2\text{NH}$ ReactionsProcess A replacement of Cl by NMe_2 B replacement of CF_3 by NMe_2

* Compounds which have been identified

compounds such as (III), arising from the elimination of the third Cl atom, were not observed.

In an attempt to gain further insight into the reaction mechanism described by eqn (5.1), $(\text{CF}_3)_2\text{PCl}_3$ was reacted with various amounts of $(\text{CH}_3)_2\text{NH}$ for only 30 minutes at room temperature. A very short reaction time was used to prevent the reaction from proceeding to completion and thereby making possible the study of any of the intermediates described in Figure 8. The volatiles from this sequence of reactions were analyzed by ir and nmr spectroscopy while the involatiles were studied exclusively by solution nmr spectroscopy in various solvents. Yields of the volatile products and recovered starting materials are given in Table XII and presented graphically in Figure 7.

The only volatiles recovered from this series of reactions were CF_3H and (I). The latter compound would arise from the stoichiometric reaction described by eqn (5.2).

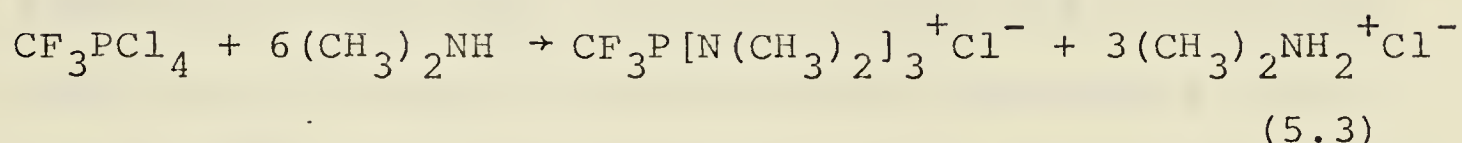


Compound (I) was produced in varying yields according to the amounts of $(\text{CH}_3)_2\text{NH}$ used and maximum yields of (I) were obtained under these reaction conditions with a $(\text{CF}_3)_2\text{PCl}_3$ to $(\text{CH}_3)_2\text{NH}$ ratio of about 1:3. The yield of

CF_3H increased regularly through the series as increasing amounts of $(\text{CH}_3)_2\text{NH}$ were used, while the amount of unreacted $(\text{CF}_3)_2\text{PCl}_3$ decreased regularly, reaching zero with a $(\text{CF}_3)_2\text{PCl}_3$ to $(\text{CH}_3)_2\text{NH}$ ratio of about 1:5. The only other CF_3P containing species identified in this series of reactions was (VI), whose formation was described by eqn (5.1). The compounds (II), (IV) and (V) are possible intermediates in this reaction scheme, whose formation can neither be confirmed nor denied since small amounts of unidentified CF_3P containing compounds were also found in the involatiles. The formation of (VI) which requires a $(\text{CH}_3)_2\text{NH}$ to $(\text{CF}_3)_2\text{PCl}_3$ ratio of 5:1 was observed even when the reacting ratios were as low as 0.8:1. The appearance of this compound under these conditions suggests that the reaction mechanism is nonhomogeneous and that it is possibly the result of a surface phenomenon.

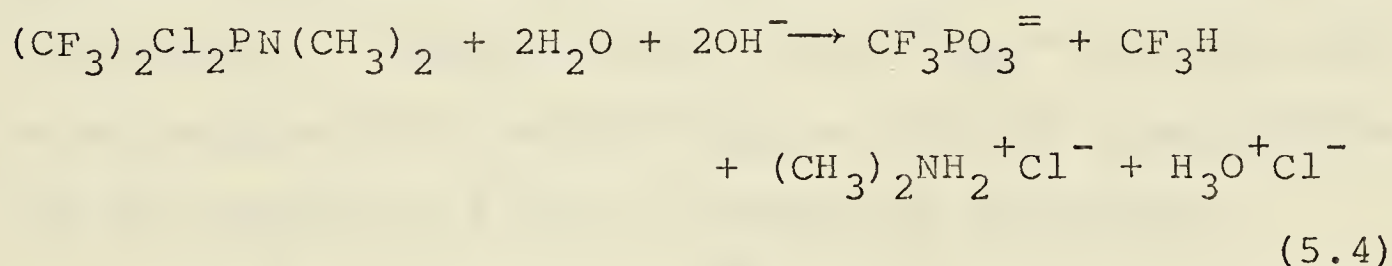
The reaction of CF_3PCl_4 with 10 molar equivalents of $(\text{CH}_3)_2\text{NH}$ at room temperature for 24 hours gave 4 molar equivalents of unreacted $(\text{CH}_3)_2\text{NH}$ and one molar equivalent of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$ (although this was not weighed it was the only CF_3P containing species found amongst the $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$). The mixture of salts obtained was shown by nmr spectroscopy to contain the same constituents as those formed from the reaction of $(\text{CF}_3)_2\text{PCl}_3$ with 6 molar equivalent of $(\text{CH}_3)_2\text{NH}$. The overall stoichiometry of

the reaction described above can be expressed by the eqn (5.3).

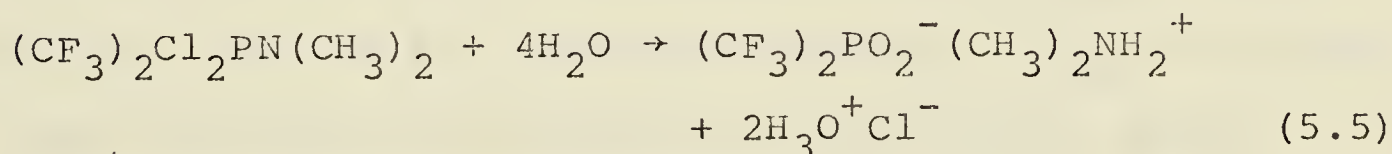


As was the case with the reactions of $(\text{CF}_3)_2\text{PCl}_3$ and $(\text{CH}_3)_2\text{NH}$, no evidence was obtained indicating substitution of the last CF_3 group on phosphorus nor substitution of the third Cl group in the reaction described above.

The alkaline hydrolysis of $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ gave one molar equivalent of CF_3H according to the eqn (5.4).



The neutral hydrolysis of $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ gave no CF_3H according to eqn (5.5).



The chemical behavior described above agrees with the proposed formulation of a bis(trifluoromethyl)phosphorus compound containing a pentavalent pentacoordinate phosphorus atom.

The ir spectrum of $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$ (Table VIII) gave the expected CF_3 and CH_3 absorptions, an asymmetric C_2N stretching vibrations at 990 cm^{-1} and three peaks at 590

cm^{-1} , 558 cm^{-1} and 536 cm^{-1} which arose from either asymmetric N_2P stretching, asymmetric CF_3 deformation or P-Cl stretching vibrations. The ion at m/e 248 in the mass spectrum was found by accurate mass measurement to be the $\text{C}_4\text{F}_6^{35}\text{ClH}_6\text{NP}^+$ ion arising from the unobserved parent $\text{C}_4\text{F}_6^{35}\text{Cl}_2\text{H}_6\text{NP}$ by loss of ^{35}Cl . The ion at m/e 239 with an isotope pattern ratio of 9:6:1 confirms the presence of 2 chlorine atoms and strongly suggests the $\text{C}_2\text{F}_6^{35}\text{Cl}_2^+$ ion.

The room temperature ^1H spectrum of (I) (Figure 9) shows a doublet of septets arising from coupling of the protons to the phosphorus atom ($^3J_{\text{PH}} = 12.5 \text{ Hz}$) and to six equivalent F atoms ($^5J_{\text{FH}} = 1.05 \text{ Hz}$) thus confirming the presence of two CF_3 groups on phosphorus.

The room temperature ^{19}F spectrum of (I) (Figure 9) shows a doublet of septets arising from coupling of the fluorine atoms to a phosphorus atom ($^2J_{\text{PF}} = 156.9 \text{ Hz}$) and also to six equivalent protons ($^5J_{\text{FH}} = 1.09 \text{ Hz}$), thus confirming the presence of one $\text{N}(\text{CH}_3)_2$ group attached to a phosphorus atom.

Reactions of CF_3PCl_4 and $(\text{CF}_3)_2\text{PCl}_3$ with excess $(\text{CH}_3)_2\text{NH}$ gave as an involatile white solid a mixture of $(\text{CH}_3)_2\text{NH}_2^+\text{Cl}^-$ and a compound with the empirical formula " $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3\text{Cl}$ ". Attempts to separate these solids by solvent extraction were unsuccessful. However, reaction of an aqueous solution of KPF_6 with the above

FIGURE 9

Proton and ^{19}F nmr spectra of $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$. The ^1H spectrum was measured at 60 MHz on a solution in CFCl_3 at 40°C . The frequency scale is measured relative to TMS with positive sign denoting resonance to lower field of standard. The ^{19}F spectrum was measured at 56.4 MHz on a solution in CFCl_3 at 40°C . In this case the frequency scale is measured relative to CFCl_3 with positive sign denoting resonance to high field of the standard. The calculated ^1H spectrum, using the parameters given in Table XIII, is shown as stick diagrams above the observed spectrum.

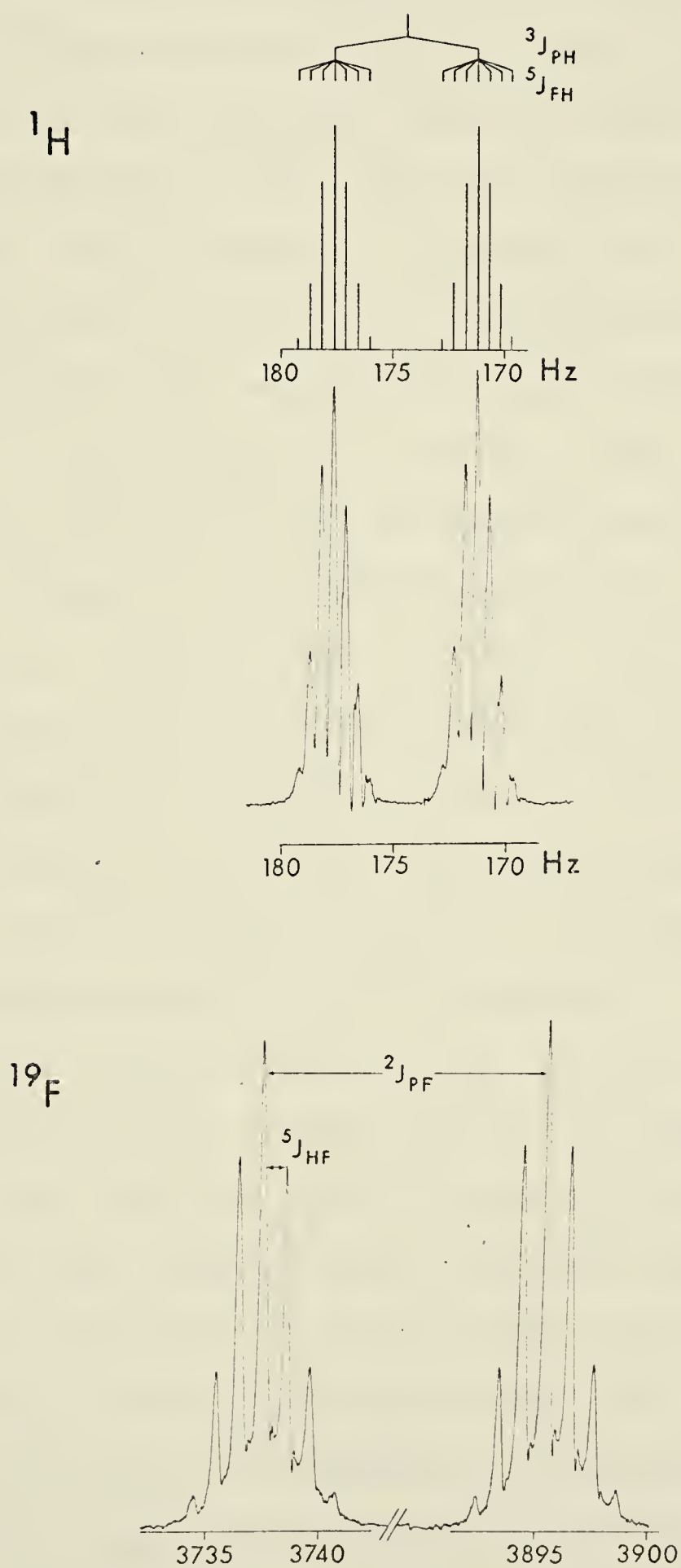
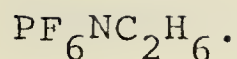


FIGURE 9. The ^1H and ^{19}F nmr Spectra of $(\text{CF}_3)_2\text{Cl}_2\text{PN}(\text{CH}_3)_2$

salt mixture gave a white precipitate. A CD_3CN solution of this white precipitate showed the same nmr parameters as a CD_3CN solution of the original salt mixture (exclusive of the $(\text{CH}_3)_2\text{NH}_2^+$ and PF_6^- signals) thus confirming the presence of the same CF_3P containing species in each case. The fluorine to hydrogen ratio of this compound was found to be 1:6 using fluorobenzene as an internal standard, thus suggesting a CF_3 to $\text{N}(\text{CH}_3)_2$ ratio of 1:3. The fluorine signal of the PF_6^- anion and the fluorine signal from the CF_3P containing compound integrated in the ratio of 2:1, indicating one CF_3 group per PF_6^- moiety. These results strongly suggested that the white precipitate was the salt $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{PF}_6^-$ which was confirmed by elemental analysis. Thus the compound with the empirical formula " $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3\text{Cl}$ " was in fact the salt $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$. Confirmation of these conclusions came from the ir spectra of these PF_6^- and Cl^- salts. These salts had very similar spectra (Table X) differing only in that additional peaks attributable to the PF_6^- and $(\text{CH}_3)_2\text{NH}_2^+$ ions were present in the former and latter respectively. The bands remaining could then all be assigned as arising from the $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+$ ion. Notably bands appearing at 1010 cm^{-1} and 652 cm^{-1} can be attributed to asymmetric C_2N and N_2P stretching vibrations. The ions appearing at m/e 277, 232 and 188 in the mass spectrum could be explaining as arising from the unobserved parent at m/e 377 by loss of C_2F_4 , PF_6 and



The alkaline hydrolysis of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{PF}_6^-$ gave one molar equivalent of CF_3H with $\text{OP}[\text{N}(\text{CH}_3)_2]_3$ and PF_6^- as the only species found in the aqueous solution. The presence of $\text{OP}[\text{N}(\text{CH}_3)_2]_3$ was confirmed by comparing its nmr spectrum with the nmr spectrum of an authentic sample of $\text{OP}[\text{N}(\text{CH}_3)_2]_3$ dissolved in water and in a 10% NaOH solution; all these solutions gave identical ^1H spectra.

The room temperature ^1H nmr spectrum of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$ showed a doublet of quartets arising from coupling of the protons to a phosphorus atom ($^3J_{\text{PH}} = 10.2 \text{ Hz}$) and to three equivalent fluorine atoms ($^5J_{\text{FH}} = 0.75 \text{ Hz}$) thus confirming the presence of one CF_3 group on the phosphorus atom.

The room temperature ^{19}F nmr spectrum of $\text{CF}_3\text{P}[\text{N}(\text{CH}_3)_2]_3^+\text{Cl}^-$ showed a doublet of broad multiplets presumably arising from coupling to a phosphorus atom ($^2J_{\text{PF}} = 108 \text{ Hz}$) and coupling to eighteen equivalent protons of the three $\text{N}(\text{CH}_3)_2$ groups splitting each component of the doublet into nineteen line multiplets. Although these multiplets could not be resolved, the peak width was in agreement with that expected from the coupling constant measured in the ^1H spectrum, and the other spectroscopic and chemical evidence described above confirms the presence of three $\text{N}(\text{CH}_3)_2$ groups.

CHAPTER VI

COLLECTED NMR DATA AND STRUCTURAL CONSIDERATIONS

In the reactions of $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$ with CH_3OH and H_2S , described in Chapter 3 it was suspected that some of the products obtained were the phosphoryl and thiophosphoryl bis(dimethylamino) compounds $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$ and $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$.⁴² Since the nmr parameters of these compounds had not been reported, the synthesis of these compounds and their monochloro analogs $\text{CF}_3\text{P}(\text{O})\text{N}(\text{CH}_3)_2\text{Cl}$ and $\text{CF}_3\text{P}(\text{S})\text{N}(\text{CH}_3)_2\text{Cl}$ is described and their nmr parameters are recorded herein.

The reaction of $(\text{CF}_3)_3\text{P}$ and Br_2 was studied at low temperature to facilitate the isolation and identification of any reaction intermediates. Experiments aimed at elucidating the low temperature stereochemical configurations of $(\text{CF}_3)_2\text{PCl}_3$, $(\text{CF}_3)_3\text{PCl}_2$ and $(\text{CF}_3)_3\text{PBr}_2$ will also be described. Finally, nmr parameters of all the new compounds prepared in this study are collected in Table XIII.

1. Preparation of $\text{CF}_3\text{P}(\text{S})\text{N}(\text{CH}_3)_2\text{Cl}$ and $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$

A sample of $\text{CF}_3\text{P}(\text{S})\text{Cl}_2$ was allowed to react with approximately 4 molar equivalents of $(\text{CH}_3)_2\text{NH}$ at room temperature for 24 hours. Vacuum fractionation of the volatile products afforded a mixture of $\text{CF}_3\text{P}(\text{S})\text{N}(\text{CH}_3)_2\text{Cl}$ and $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$ ⁴² (identified by nmr spectroscopy and mass spectroscopy) which trapped at -45°C . Small

amounts of unreacted $(\text{CH}_3)_2\text{NH}$ were recovered in the -116°C trap.

2. Preparation of $\text{CF}_3\text{P}(\text{O})\text{N}(\text{CH}_3)_2\text{Cl}$ and $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$

The compound $\text{CF}_3\text{P}(\text{O})\text{Cl}_2$ was allowed to react with approximately 4 molar equivalents of $(\text{CH}_3)_2\text{NH}$ at room temperature for 24 hours. Vacuum fractionation gave a mixture of $\text{CF}_3\text{P}(\text{O})\text{N}(\text{CH}_3)_2\text{Cl}$ and $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$ (identified by nmr spectroscopy) which trapped at -45°C . Small amounts of unreacted $(\text{CH}_3)_2\text{NH}$ were also recovered.

3. Preparation of $(\text{CF}_3)_3\text{PBr}_2$

A sample of $(\text{CF}_3)_3\text{P}$ and Br_2 (in a 1:1.4 ratio) was frozen into a nmr tube at -196°C and slowly allowed to warm to room temperature. At -70°C , -50°C and -30°C , the only peaks in the ^{19}F nmr spectrum arose from $(\text{CF}_3)_3\text{P}$. At -10°C a doublet ($J = 128 \text{ Hz}$, $\phi_{\text{F}} = 65.8 \text{ ppm}$) was observed in the ^{19}F nmr spectrum with a concurrent decrease in the intensity of the signal arising from $(\text{CF}_3)_3\text{P}$. The nmr tube was then warmed to room temperature for 30 seconds allowing thorough mixing of the two components. The colourless upper portion (presumably $(\text{CF}_3)_3\text{P}$) and the lower red portion (presumably Br_2) mixed to form a homogeneous light orange solution. The ^{19}F nmr spectrum of this homogeneous solution indicated the presence of $(\text{CF}_3)_2\text{PBr}_3$ ⁴⁹, CF_3Br ⁵⁰, $(\text{CF}_3)_3\text{P}$ and an unknown compound,

presumably $(\text{CF}_3)_3\text{PBr}_2$, with the nmr parameters mentioned above. After 24 hours at room temperature, the signals attributed to $(\text{CF}_3)_3\text{PBr}_2$ ²⁵ had disappeared with $(\text{CF}_3)_2\text{PBr}_3$, CF_3Br and $(\text{CF}_3)_3\text{P}$ as the only CF_3 containing species in solution.

4. Results and Discussion

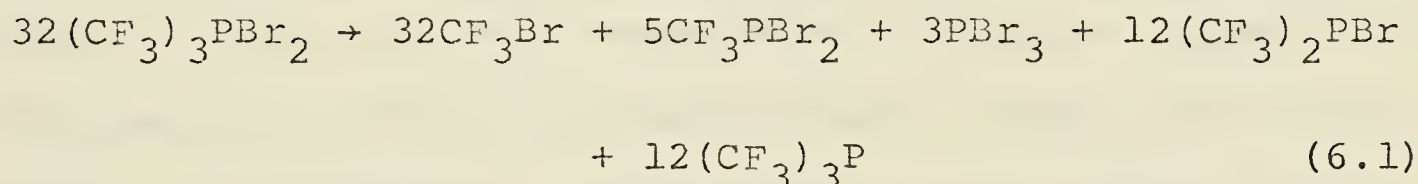
The reaction of $\text{CF}_3\text{P}(\text{S})\text{Cl}_2$ with approximately 4 moles of $(\text{CH}_3)_2\text{NH}$ resulted in the formation of a mixture of two compounds. The compounds $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2$ (I) and $\text{CF}_3\text{P}(\text{S})\text{N}(\text{CH}_3)_2\text{Cl}$ (II) are relatively involatile liquids and were studied as an unseparated mixture, however, the signals in their nmr spectra were well separated and easily analyzed. The room temperature ^1H nmr spectra of (I) and (II) show a doublet of quartets arising from coupling to a phosphorus atom ($^3\text{J}_{\text{HP}} = 12.0 \text{ Hz}$, 13.6 Hz respectively) and to three equivalent fluorine atoms ($^5\text{J}_{\text{FH}} = 0.75 \text{ Hz}$ in each case) thus confirming the presence of one CF_3 group on phosphorus. The room temperature ^{19}F nmr spectrum of (I) shows a doublet of either 11 or 13 line multiplets with an intensity distribution in good agreement with that expected for the central 11 lines of a 13 line pattern. This spectrum is generated by coupling to a phosphorus nucleus ($^2\text{J}_{\text{FP}} = 93.7 \text{ Hz}$) and twelve equivalent protons ($^5\text{J}_{\text{FH}} = 0.75 \text{ Hz}$) indicating the presence of two $\text{N}(\text{CH}_3)_2$ groups on the phosphorus atom. The room

temperature ^{19}F nmr spectrum of (II) shows a doublet of septets arising from coupling to a phosphorus atom ($^2J_{\text{FP}} = 121.8 \text{ Hz}$) and to six equivalent protons ($^5J_{\text{FH}} = 0.75 \text{ Hz}$) confirming the presence of one $\text{N}(\text{CH}_3)_2$ group on phosphorus. The mass spectra of (I) and (II) showed the parent ions which were identified by accurate mass measurement (calcd for $\text{CF}_3\text{P}(\text{S})\text{N}(\text{CH}_3)_2^{35}\text{Cl}^+$ m/e 210.9599; found m/e 210.9605; calcd for $\text{CF}_3\text{P}(\text{S})[\text{N}(\text{CH}_3)_2]_2^+$ m/e 220.0409; found m/e 220.0404).

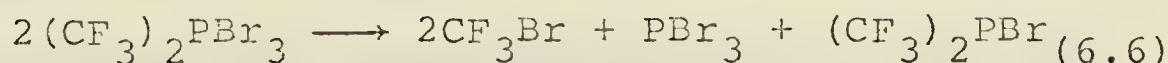
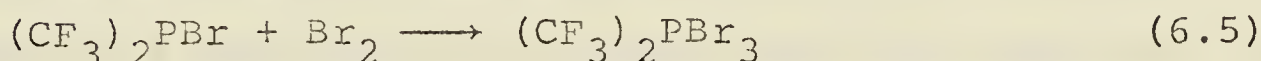
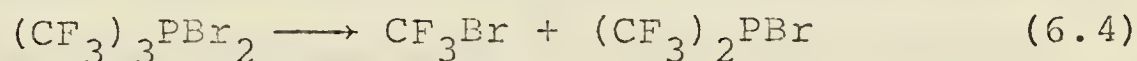
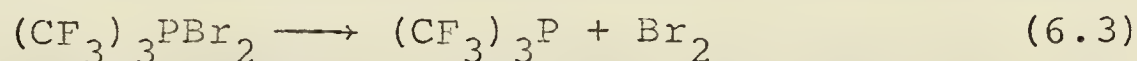
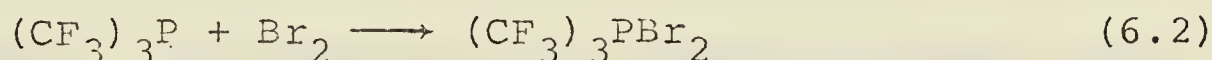
The reaction of $\text{CF}_3\text{P}(\text{O})\text{Cl}_2$ with $(\text{CH}_3)_2\text{NH}$ resulted similarly in the formation of a mixture of $\text{CF}_3\text{P}(\text{O})[\text{N}(\text{CH}_3)_2]_2$ (III) and $\text{CF}_3\text{P}(\text{O})\text{N}(\text{CH}_3)_2\text{Cl}$ (IV) as liquids of low volatility possessing distinct separated nmr signals. The room temperature ^1H spectra of (III) and (IV) show a doublet of quartets arising from coupling to a phosphorus atom ($^3J_{\text{HP}} = 9.95 \text{ Hz}$, 12.05 Hz respectively) and to three equivalent fluorine atoms ($^5J_{\text{FH}} = 0.70 \text{ Hz}$ in each case) confirming the presence of one CF_3 group on phosphorus. The room temperature ^{19}F nmr spectrum of (III) showed a doublet of asymmetric multiplets containing at least 10 lines which was generated by coupling to a phosphorus atom ($^2J_{\text{FP}} = 96.0 \text{ Hz}$) and to (presumably) twelve protons ($^5J_{\text{FH}} = 0.70 \text{ Hz}$) suggesting the presence of two $\text{N}(\text{CH}_3)_2$ groups on phosphorus. The room temperature ^{19}F nmr spectrum of (IV) shows a doublet of septets arising from coupling to phosphorus ($^2J_{\text{PF}} = 126.4 \text{ Hz}$) and to six equivalent protons ($^5J_{\text{FH}} =$

0.70 Hz) confirming the presence of one $\text{N}(\text{CH}_3)_2$ group on phosphorus.

Reactions of some trifluoromethylphosphines with bromine have been investigated by Burg and Griffiths.²⁵ The phosphines $(\text{CF}_3)_n\text{PBr}_{3-n}$ ($n = 1, 2$) gave the phosphoranes $(\text{CF}_3)_n\text{PBr}_{5-n}$ ($n = 1, 2, 3$) but $(\text{CF}_3)_3\text{PBr}_2$ could not be isolated, being unstable under the conditions of the experiment. Specifically, after 9 hours at 90°C , the reaction of equimolar quantities of $(\text{CF}_3)_3\text{P}$ and Br_2 gave products corresponding to the overall empirical equation (6.1)²⁵



and evidence was presented showing that this resulted from the sequence of reactions²⁵ (6.2-6.6).



The products were analyzed and identified by ir spectroscopy, CF_3H and Volhard analyses and tensiometric determinations, but no nmr data was reported. In an attempt to

confirm the presence of this intermediate $(\text{CF}_3)_3\text{PBr}_2$ and obtain nmr evidence for these proposed sequences, samples of $(\text{CF}_3)_3\text{P}$ and Br_2 in a 1:1.4 ratio were frozen into an nmr tube at -196°C and slowly warmed. At -10°C the initially immiscible liquids reacted slowly to generate a compound, presumably $(\text{CF}_3)_3\text{PBr}_2$, with ^{19}F nmr parameters ($J = 128 \text{ Hz}$, $\phi_{\text{F}} = 65.8 \text{ ppm}$) which are well within the typical range of nmr parameters for known tri-fluoromethylphosphoranes. After 30 seconds at room temperature the known signals arising from the decomposition products $(\text{CF}_3)_2\text{PBr}_3$, CF_3Br , $(\text{CF}_3)_3\text{P}$ as well as the above signals attributed to $(\text{CF}_3)_3\text{PBr}_2$ were present. However, after 24 hours at room temperature the latter signals had disappeared leaving only the signals arising from the decomposition products. Thus we have quite clearly demonstrated that $(\text{CF}_3)_3\text{PBr}_2$ is an intermediate in the reaction of $(\text{CF}_3)_3\text{P}$ and Br_2 (eqn 6.2). Its formation occurs above -10°C but suffers fairly rapid decomposition at room temperature. The decomposition products observed could result from the sequence of reactions (6.4 and 6.5). In contrast with the previous work ²⁵ $(\text{CF}_3)_2\text{PBr}$ was not observed as a decomposition product and thus reaction (6.6) may not be significant decomposition mode at this temperature. Also no evidence for decomposition by reaction (6.3) was obtained, since all the $(\text{CF}_3)_3\text{P}$ need not have reacted to form $(\text{CF}_3)_3\text{PBr}_2$ initially.

Pseudorotatory processes are known to occur in many phosphoranes and have been shown by nmr spectroscopy to be occurring in some of the trifluoromethylphosphoranes discussed in this study. In most of these compounds the apicophilicity of the groups present is such that groups exhibit a definite preferred orientation. Attempts were made to study these pseudorotatory processes in trifluoromethylhalophosphoranes containing substituents with relatively similar apicophilicity. Thus dilute solutions of $(\text{CF}_3)_3\text{PCl}_2$, $(\text{CF}_3)_3\text{PBr}_2$ and $(\text{CF}_3)_2\text{PCl}_3$ were investigated by ^{19}F nmr spectroscopy at temperatures ranging from 40°C to -140°C . In all these halophosphoranes the more electronegative and less effective π donating CF_3 group would be expected to occupy axial orientations as much as possible. This would leave one CF_3 and two halogen groups in the equatorial positions in $(\text{CF}_3)_3\text{PX}_2$ ($\text{X} = \text{Br}, \text{Cl}$) and three chlorine groups in these positions in $(\text{CF}_3)_2\text{PCl}_3$. Thus slowing down (by cooling) of these pseudorotatory processes should give rise to two chemically shifted regions of relative intensity 2:1 in the former two cases but no such separation in the latter case.

In all three cases no evidence was found for any such separation or even broadening of signals at -140°C . It is possible to interpret these results as arising from three equivalent equatorial groups in the $(\text{CF}_3)_3\text{PX}_2$ ($\text{X} = \text{Cl}, \text{Br}$) cases and two equivalent axial

CF_3 groups in $(\text{CF}_3)_2\text{PCl}_3$. However, it is also possible that even at -140°C the pseudorotation processes are still occurring at a rate fast enough as to result in chemical equivalence and thus indicating the low energy barrier to rotation of such processes.

The low temperature nmr studies have indicated that the axial sites in $(\text{CF}_3)_3\text{P}[\text{N}(\text{CH}_3)_2]_2$, $(\text{CF}_3)_3\text{P}(\text{Cl})\text{N}(\text{CH}_3)_2$ and $(\text{CF}_3)_2\text{FP}[\text{N}(\text{CH}_3)_2]_2$ are occupied in the first case by two CF_3 groups, in the second case by one CF_3 and one Cl group and in the third by one CF_3 and one F group. The large room temperature ^{19}F nmr coupling constants of $(\text{CF}_3)_2\text{F}_2\text{P}[\text{N}(\text{CH}_3)_2]_2$ and $(\text{CF}_3)_2\text{PCl}_2\text{N}(\text{CH}_3)_2$ strongly suggest that two F atoms and two Cl atoms respectively, occupy axial sites. Neither the electronegativity nor the π donor ability of these groups can satisfactorily explain these observations. The one trend that is observable throughout the series is the strong apicophilic behavior of the halogen substituent.

TABLE XIII

Summary of the NMR Parameters of the Compounds Prepared in this Study

<u>Compound</u>	<u>ϕ_F^a</u>	<u>τ_H^b</u>	<u>$2J_{FP}$</u>	<u>$3J_{HP}$</u>	<u>$5J_{FH}$</u>	<u>$1J_{FP}$</u>	<u>$4J_{FH}$</u>	<u>$3J_{FF}$</u>	<u>$4J_{FF}$</u>	<u>Notes</u>
$CF_3P(S) [N(CH_3)_2]_2$	67.6	7.49	94.7	12.0	0.75					
$CF_3P(S)Cl[N(CH_3)_2]$	73.1	7.18	121.8	13.6	0.75					
$CF_3P(O)[N(CH_3)_2]_2$	67.5	7.48	96.0	9.95	0.70					
$CF_3P(O)Cl[N(CH_3)_2]$	73.6	7.28	126.4	12.05	0.70					
$CF_3PO_3H^-$	73.5		107							In H ₂ O
$CF_3P[N(CH_3)_2]_3^{+}Cl^{-}$	60.8	7.20	108	10.2	0.79					In CD ₃ CN
$(CF_3)_3PBr_2$	65.8		128							
$(CF_3)_3P[N(CH_3)_2]_2$	56.7 57.0	7.05	c 50.5	11.6	0.95				16.5	At -30° in CF ₂ Cl ₂ 2CF ₃ ax 1CF ₃ eq
	55.6 53.9		108 71							At 75° in C ₆ F ₆
$(CF_3)_3PCl[N(CH_3)_2]$	59.1 59.3 57.7	7.20	105.5 130 ~53	13.9	0.68					At 40° { At -120° in CF ₂ Cl ₂ . 2CF ₃ eq CF ₃ ax
$(CF_3)_2PCl_2[N(CH_3)_2]$	67.8	7.17	156.9	12.5	1.09					

(continued.....)

TABLE XIII (continued)

$(\text{CF}_3)_2\text{PF}[\text{N}(\text{CH}_3)_2]_2$	58.2	7.43	88	11.6	0.60	792	3.1	{ At 40°
	32.6							
	61.4		125.5					
	56.2		C					
	49.6		C					
$\text{CF}_3\text{PF}_2[\text{N}(\text{CH}_3)_2]_2$	59.9		86			794	2.7	{ At 75° in C_6F_6
	68.6	7.44	150	10.1	~0			
	58.9							
$(\text{CF}_3)_2\text{P}(\text{CCl}_3)[\text{N}(\text{CH}_3)_2]_2$	60.8	6.81	115	10.9	0.62	794	2.7	{ At -90° CF_3eq in CF_2Cl_2 2Fax 1Fax
$(\text{CF}_3)_2\text{P}(\text{CCl}_2\text{H})[\text{N}(\text{CH}_3)_2]_2$	70.1	7.33	106	10.5		794	2.7	{ At 75° in C_6F_6

(a) Spectra were recorded as dilute solutions in CFCl_3 unless otherwise stated. Chemical shifts are given in ppm upfield from CFCl_3 , in solvents other than CFCl_3 , the chemical shifts were recorded relative to external CFCl_3 .

(b) Signals recorded relative to external TMS.

(c) Signals are broad multiplets.

REFERENCES

1. E. L. Muetterties and R. A. Schunn, *Quart. Revs.*, 245 (1966).
2. P. C. Van der Voorn and R. Drago, *J. Amer. Chem. Soc.*, 88, 3255 (1966).
3. E. L. Muetterties, *Accounts Chem. Res.*, 3, 266 (1970).
4. I. Ugi, D. Marguarding, H. Klusacek, P. Gillespie and F. Ramirez, *Accounts Chem. Res.*, 4, 288 (1971).
5. J. B. Florey and L. C. Cusachs, *J. Amer. Chem. Soc.*, 94, 3040 (1972).
6. R. Hoffman, J. M. Howell and E. L. Muetterties, *J. Amer. Chem. Soc.*, 94, 3047 (1972).
7. J. Zemann, *Z. Anorg. Allgem. Chem.*, 324, 241 (1963).
8. R. Schmutzler, *Angew. Chem. Internat. Edit.*, 4, 496 (1965).
9. R. J. Gillespie, *J. Chem. Educ.*, 47, 18 (1970).
10. D. P. Craig, R. S. Nyholm, A. MacColl, L.E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).
11. E. L. Muetterties, W. Mahler and R. Schmutzler, *Inorg. Chem.*, 2, 613 (1963).
12. G. O. Doak and R. Schmutzler, *Chem. Comm.*, 476 (1970).
13. M. Becke-Goehring and H. Weber, *Z. Anorg. Chem.*, 365, 185 (1969).
14. P. Gillespie, P. Hoffman, H. Klysacek, D. Marguarding, S. Pfohl, F. Ramirez, E. A. Tsolis and I. Ugi, *Angew. Chem. Internat. Edn.*, 10, 687 (1971).

15. R. K. Oramond, S. Trippett, Chem. Comm., 554 (1972).
16. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd Edition, Interscience, 1966.
17. J. E. Huheey, J. Phys. Chem., 69, 3284 (1965).
18. P. R. Wells, S. Ehrenson and R. W. Taft, in "Progress in Physical Organic Chemistry", Vol. 6, Interscience 1968.
19. I. Ugi and F. Ramirez, Chem. Brit., 8, 198 (1972).
20. F. W. Bennett, H. J. Emeléus, and R. N. Haszeldine, J. Chem. Soc., 1565 (1953).
21. H. J. Emeléus, R. N. Haszeldine and R. C. Paul, J. Chem. Soc., 563 (1955).
22. J. E. Griffiths and A. L. Beach, J. Chem. Phys., 44, 2686 (1966).
23. W. Mahler and A. B. Burg, J. Amer. Chem. Soc., 80, 6161 (1958).
24. J. E. Griffiths, J. Chem. Phys., 41, 3510 (1964).
25. A. B. Burg and J. E. Griffiths, J. Amer. Chem. Soc., 82, 3514 (1960).
26. W. Mahler, Inorg. Chem., 2, 230 (1963).
27. J. E. Griffiths, J. Chem. Phys., 49, 1307 (1968).
28. E. A. Cohen and C. D. Cornwall, Inorg. Chem., 7, 398 (1968).
29. J. E. Griffiths, Inorg. Chim. Acta, 1, 127 (1967).
30. H. G. Ang, Chem. Comm. 1320 (1968).
31. H. G. Ang, J. Inorg. Nucl. Chem. Lett., 31, 3311 (1969).

32. J. F. Nixon, J. Inorg. Nucl. Chem. Lett., 31, 1615 (1969).
33. R. G. Cavell, R. D. Leary, A. J. Tomlinson, Inorg. Chem., 11, 2578 (1972).
34. S. S. Swain and P. M. Treichel private communication.
35. A. B. Burg, W. Mahler, A. J. Bilbo, C. P. Haber and D. L. Herring, J. Amer. Chem. Soc., 79, 247 (1957).
36. G. S. Harris, J. Chem. Soc., 512 (1958).
37. T. A. Blazer, R. Schmutzler, and I. K. Gregor, Zeit. Naturforsch., 24b, 1081 (1969).
38. A. A. Pinkerton and R. G. Cavell, Inorg. Chem., 10, 2720 (1971).
39. J. F. Nixon and R. G. Cavell, J. Chem. Soc., 5983 (1964).
40. R. G. Cavell and H. J. Emeleus, J. Chem. Soc., 5825 (1964).
41. G. R. Petit, I. B. Irwin and R.A. Hill, Can. J. Chem., 42, 2357 (1964).
42. K. Gosling and A. B. Burg, J. Amer. Chem. Soc., 90, 2011 (1968).
43. R. C. Dobbie, L. F. Doty and R. G. Cavell, J. Amer. Chem. Soc., 90, 2015 (1968).
44. H. J. Emeléus, R. N. Haszeldine, and R. C. Paul, J. Chem. Soc., 563 (1955).
45. F. W. Bennett, H. J. Emeléus and R. N. Haszeldine, J. Chem. Soc., 3896 (1954).

46. M. G. Barlow, R. Fields and F. P. Temme, Chem. Comm.
1671 (1968).
47. G. W. Parshall and F. N. Jones, J. Amer. Chem. Soc., 87,
5356 (1965).
48. D. H. Brown, G. W. Fraser and D. W. A. Sharp, Chem.
Ind., 367 (1964).
49. R. G. Cavell and A. A. Pinkerton, unpublished results.

B30049